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Surface modification of Si-based materials by plasma gas treatments

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Abstract

As the key material of microelectronic technology, silicon has gradually been recognized as an essential element and tremendous technical development has been undergone. An increasing number of silicon-containing materials are being investigated as the potential materials for the application in the field of microelectronics, photonics, and biomedical devices and so on. Among of them, the surface properties of these Si-based materials are one of the key elements.
to decide the performance of the corresponding devices. Therefore, surface modification has become an interesting topic as an effective means to improve the surface functions of Si-based materials. In the past several decades, plasma surface modification (PSM) has been widely used in industrial treatment to clean or improve the properties of materials surface. Plasma treatment not only chemically and/or physically alters the surface composition and microstructures via processes such as etching, chemical reactions, sterilization, ion irradiation and bombardment, but also can synthesize a different structure such as a thin film on the surface of the Si-based materials via coating, grafting, and thin film deposition. The new film or surface can possess very different chemical and physical properties than the bulk materials. In this chapter, the surface modification of Si-based materials by gas plasma treatments such as H₂ is described. A number of the examples are presented such as single-crystalline silicon, amorphous silicon, porous silicon, and silicon carbide. In all of these cases, the aim of surface treatment is to improve the surface chemical bonding nature of the coating or films. The physical, chemical, electrical, and biological properties of Si-based materials by various plasma gas treatments are evaluated.

1. Introduction
1.1. Silicon and Si-based materials

The discovery and utilization of semiconductors, particularly of silicon, revolutionized our living conditions, society, social life, and maxims in a few decade years, even more than what happened during all the material-specified periods before. Perhaps, one day, our descendants will call the period at whose beginning we live the Silicon Age. As the base materials for electronics, silicon plays a central role of the interdependencies for the utilization. Since the first intensive work on silicon started more than 50 years ago, silicon has been all around us in terms of electronic devices. Silicon is the quintessential electronic material. It is often said that understanding silicon and its role in electronic materials is similar to understanding iron and its role in metallurgy and making steel [1-3]. The influence of industrial mass production of high-grade, single-crystal silicon on the development of our civilization was and is unique in the whole history of mankind: computers, communication systems, sensors, medical equipments, photovoltaics, satellites, space shuttles, etc.

Silicon is by far the most widely used semiconductor material. It is abundant in the earth’s crust and relatively easy to convert into a high-purity single crystal. Unlike some other semiconductor materials, silicon is stable when heated at high temperature, and a well-behaved insulating and passivating material, silicon dioxide, can readily be grown on it. The excellent
electrical and chemical properties of thermally grown SiO₂ are probably the most important factor that has made silicon such a successful semiconductor material. Silicon occurs in the diamond structure, with the lattice constant \( a_0 = 0.543 \, \text{nm} \). This corresponds to the density of \( 5.0 \times 10^{22} \, \text{atoms/cm}^3 \), as shown in Fig.1. Within the primitive cell, there are eight electrons, which mean there
are four occupied valence bands [4]. Shown in Fig.2 are the energy bands for silicon in the diamond crystal structure [5]. This represents one of the first realistic energy-band structures. In silicon, the bandgap is about 1.1 eV and the valence-band width is about 12 eV. Silicon does not appear as a free element in nature, because of its high chemical affinity, especially for oxygen. It can only be produced by chemical reduction.

Silicon, with all its positive basic attributes, had first to be made readily available for large-scale common use. This was an often difficult path into the unknown, where only the human pioneering spirit had a chance to overcome all the difficulties that were encountered. It certainly was not as straightforward development- as it might appear to someone in retrospect and as extrapolations such as Moore’s Law might make one believe- but rather one that was characterized by many, often extremely complex individual developments [6, 7]. It was an outstanding achievement of the human spirit in research, as well as of interdisciplinary cooperation between material researchers, device developers, designers, and technologists.

Most importantly, it is obvious that a uniform, high-purity, perfect single-crystal piece of silicon material alone would be of extremely limited technological use. It is only when this material is suitably altered and structured through controlled, reproducible processes and then made into useful devices that it becomes valuable. All of these requirements could not have been achieved were it not for the fact that nature provided us with an extraordinary gift, through suitable physical properties and constants, etc.- an abundance of wonderful, often crucial properties and characteristics of silicon, silicon dioxide, and the Si-SiO₂ interface that, together, make modern integrated silicon technology possible at all. The most important properties and characteristics of silicon are enumerated as follows [8]:

Single crystal: with ever larger rod diameters (30 cm). Defects can be eliminated or selectively utilized for advantage.

Not brittle: can easily be handled and is an excellent mechanical substrate for individual devices and integrated circuit chips.

Adequate thermal conductivity to take away the electrically generated heat in chips.

Can be microstructured by a combination of suitable optical and chemical methods (lithography), even breaking through the 0.1 micron barrier.

Thin crystalline silicon films with various electrical properties can be grown onto insulators (sapphire, etc.) to provide improved isolation and speed, and lower capacitance.

Buried thin films of SiO₂ can be created under the silicon surface by oxygen ion implantation and subsequent annealing.

Has a very useful energy gap (1.12 eV).
Conductivity can be tailored (n-type, p-type, value) by doping using diffusion and/or ion implantation.

As an elemental semiconductor, it does not have the multitude of materials problems and chemical behavior that compound semiconductors have. Carrier mobility is good for both electrons and holes (important in CMOS circuits).

Carrier lifetime for both electrons and holes is good because of special band structure properties and low density of traps (important of bi-polar devices).

Not light-sensitive (stable operation of devices under various light conditions).

1.2. Surface structure and properties

As for the surface of silicon materials, a periodic system perpendicular to the surface no longer occurs and threefold-coordinated Si atoms at the surface, in contrast with fourfold-coordinated atoms within the bulk crystal. No the same atomic structure or the same electronic configuration at the surface is that in the bulk. If we examine the distributions of electronic charge at the surface (Fig.3) [9], we notice that the surface perturbation heals very quickly; the darker shades of gray regions indicating covalent bonds (which are missing at the surface) are restored ("healed") a short distance below the surface. Within

![Image](image_url)

**Figure 3.** The distributions of electronic charges at the surface of silicon [9].
a few bond lengths, the charge density assumes the same distribution as it had in the infinite crystal. Correspondingly, one new electronic feature exists at the surface, namely, electronic states that occur at the vacuum-solid interface. Called surface states, they decay both into the vacuum and into the bulk crystal. Electrons occupying such states are "trapped" at the interface between the crystal and vacuum. These surface states arise from dangling bonds that occur because unsaturated bonds are present at the surface. When adsorbate atoms interact with the silicon surface, the nature of the chemical bond between the adsorbate and the surface will be largely determined by the presence of these surface states.

Thus, surface studies can be helpful here not only because many technological steps depend on surface processes, but also because observations of surface structures and dynamics may help to gain insight into less accessible bulk processes. In practices, this means that such physical processes as diffusion and chemical reactions must be understood and approximately described in the language of easily solvable differential equations. Thus, starting from an analysis of atomic structures and processes, one would formulate mesoscopic models which can be treated, for example, by Monte Carlo calculations, and complete the chain by providing a predictable and transferable model for a standard industrial process simulator. Such a task must begin with studies of the relevant materials (silicon matrix and individual atoms, oxygen, hydrogen, and so on) and external atoms acting with the silicon surfaces and so on.

1.3. Reasons for surface modification

Plasma surface modification (PSM) not only chemically and/or physically alters the surface composition and microstructures via processes such as etching, chemical reactions, sterilization, ion irradiation and bombardment, but also can synthesize a different structure such as a thin film on the surface of the Si-based materials via coating, grafting, and thin film deposition [10, 11]. The new film or surface can possess very different electrical, chemical and biological properties than the bulk materials. In these ways, the surface of the Si-based materials can be made more biocompatible while the favorable bulk attributes such as strength can be retained. During the last few years, plasma treatment has been widely adopted as surface treatment, etch, and deposition processes in many industrial applications [12-14]. The large variety of surface modification as well as minimum pollution and low process cost are of the reasons for the strongly growing interest in this technique.

In this chapter, common gas plasma techniques and the properties of plasma-treated Si-based materials are described. A number of the examples are related to Si-based materials that are the most widely accepted materials in
microelectronic and medical devices such as biosensors. In all of these cases, the aim of surface treatment is to improve the surface chemical bonding nature of the coating or films. The physical, chemical, electrical, and biological properties of Si-based materials such as single-crystal silicon, amorphous silicon, porous silicon, and silicon carbide by hydrogen plasma treatments are evaluated.

2. Experimental methods of surface modifications

2.1. Plasma-surface interactions

The interactions between plasma particles and sample surface are critically dependent on the working pressure, plasma parameters and mode of operations. In general, both chemical and physical interactions have a significant effect on the outcome of the plasma treatment. Ion irradiation induces so-called ion clusters which are formed one for each incident ion and composed of vacancies, interstitials, implanted atoms, and their composites as shown in Fig. 4. Because of the lack of periodicity, the ion clusters usually show peculiar properties such as high resistivity, enhanced or retarded etching rate in chemical etchants. For doping effects, heat treatment is necessary to recover disorder and locate the implanted atoms in substitutional sites. Defect formation and electrical activation have been the major concern in ion implantation technology which has played an essential role in extremely high

![Figure 4. Schematic of ion-solid interactions, the sputtering process.](image-url)
integration. The plasma-surface interactions in ion implantation and thin film deposition process are briefly described here and readers are urged to peruse other references for more in-depth discussions [15-17].

2.2. Plasma ion implantation

The important considerations in any description of ion-solid interactions are the depth distribution of the implanted ions, irradiation damage and sputtering, creation of new materials, and ion alloying. The implanted ion penetrates a solid and comes to rest via electron and nuclear energy loss resulting in collision cascades. Those collisions can cause sputtering, radiation enhanced diffusion, ion backscattering, ion induced chemical reactions and defect generation. Sputtering sets the limit of the maximum concentration of implanted atoms that can be retained in the target. The yield of sputtered atoms, that is, the number of sputtered atoms per incident ion, typically varies from 0.5 to 20 depending upon the primary ion species, ion energy, structure and composition of the target, and sample topography. As ion irradiation is quite efficient in forming vacancy-interstitial pairs, the effects of irradiation on the ordered alloy are described by the competing processes of chemical disordering which is induced by atomic replacements resulting from displacement and cascade damage and chemical ordering. The process is stimulated by radiation enhanced diffusion. Besides, ion implantation offers the ability to alloy any elemental species into the near-surface region of any substrate, irrespective of thermodynamic criteria such as solubility and diffusivity. These considerations coupled with the possibility of low-temperature processing have prompted explorations into applications where the limitations of dimensional changes and possible delamination associated with conventional coatings are practical concerns.

In plasma implantation, ions in the overlying plasma are accelerated by a high field towards the material surface for structures and properties modification [18]. Generally, the ion penetration depth is a function of the implantation energy and also depends on the material properties such as electrical conductivity and density. The physical changes arise from atomic and nuclear collisions often leading to formation of highly disordered and sometimes amorphous structures. Chemical changes arise from the formation of hard-phase precipitates or surface alloys. The physical and chemical changes typically combine to create surfaces that are harder and more resistant to wear and chemical attack without substantially altering the bulk properties. Besides, the use of energetic ions and activated species in the ion implantation process introduces deeper ion penetration, cross-linking, and/or chain scission. It can also enhance or reduce the functional groups on the surfaces. This may thus help reduce the aging effects and degradation of the functional groups or
chains. In addition, surface properties such as surface hardness, wear resistance, surface wettability, and surface tension can be modified [10].

2.3. Plasma sputtering and etching

In plasma sputtering and etching processes, materials are removed from the surface by chemical reactions and/or physical sputtering. Commonly, inert gases such as neon and argon are used as the carrier gas and responsible for physical ablation while reactive plasma is employed for chemical etching of the surface. The plasma used in the process generally is produced by radio frequency glow discharge (RFGD). The sputtering rate depends on the input power of the source, working pressure, and voltage applied to the substrate.

Plasma etching is a useful method to change the surface morphology of materials. For instance, polymeric materials such as polyurethane can be treated in an argon (Ar) and sulfur dioxide (SO₂) plasma to increase the surface wettability. The fibrinogen adsorption rate is reduced due to the etching effect that renders the surface rougher. This process can also be used to create the desirable micro-features and macro-features on the biomaterials. These features are capable of regulating cell functions such as repellency, proliferation, differentiation and apoptosis. The effects of the substratum topography on the cellular behavior such as cell orientation, migration and cytoskeletal arrangements have attracted much attention. Investigations of grooved surface reveal that cells aligned to the long axis of the grooves, often with organization of actin and other cytoskeletal elements in an orientation parallel to the grooves [19]. As cell behaviors such as size, shape, density and geometry can provide regular signals for cell survival and growth or apoptosis, the effectiveness of cell culturing and spreading rather than rounding on the specialized surface feature can modulate or switch cells from apoptosis to survival and growth [20]. With regard to plasma-induced surface patterning and cell culturing, Schroder, et al. [21] have introduced a plasma-etching process to induce micropatterning on polymeric materials surfaces as illustrated in Fig. 5. Their results show that ammonia plasma introduces amino groups to the surface to attain good cell adhesion whereas hydrogen plasma can be used for surface passivation. The latter process can be used to remove surface functional groups and consequently, a higher degree of cell repellence is obtained. Braber, et al. [22] have produced micro-gradient textures on titanium and silicon rubber substrates for rat dermal fibroblasts (RDFs) culturing. The RDFs cellular behavior depends on the size of the grooves and the proliferation rate of the RDFs is much higher on titanium than silicon rubber substrate. Other studies on surface activation of polyetheretherketone (PEEK) reveal that the surface topography can become irregular with high roughness, and inflammatory cell responses can be spatially controlled in a
manner that can be ultimately exploited to improve the biocompatibility of medical devices [23]. Hence, the plasma-based surface patterning technique enables visualization of the effects on cell functions and spatially controls the cellular micro-organization.

2.4. Thin film deposition

In this process, reactants diffuse from the plasma to the substrate surface giving rise to chemical reactions and thin film deposition as shown in Fig. 6. Deposition process parameters such as the type of ions and their energy, flux, incident direction, and deposition temperature play important roles in the film composition, structure and many related properties such as grain size, crystallographic orientation, defects, stress concentration, film adhesion, and surface topography, all of which alter the mechanical, electrical, optical, as well as biomedical properties of the materials. Under certain ion energy
Figure 6. Schematic diagram of the sequential steps of deposition process.

bombardment, various surface features and microstructures such as cones, pyramids, ridges, ledges, pits and faceted planes can form. It should also be noted that under ion bombardment, films frequently show preferred orientation. In the case of low atom mobility or low substrate temperature, films have a tilted, voided columnar structure and ion bombardment generally causes a reduction in the film grain size [24]. Energetic ions displacing atoms from equilibrium sites lead to a small grain as well as a defective and stressful film. The threshold ion energies and critical temperatures often delineate the limits of the competition between lattice damage and defect annealing effects. Therefore, a proper set of plasma parameter and deposition conditions is important to yield desirable film structure and properties.

3. Surface activation of materials by plasma treatments
3.1. Single-crystal silicon
3.1.1. Background

Single-crystal silicon ULSI devices today have a feature size of a few nm and are confronted with many issues due to nm size [6]. For example, in nanoscale devices, device size becomes comparable to the average distance between dopant atoms and the assumption of uniform dopant distribution is no longer valid. In this situation, the statistical fluctuation in dopant atom number due to random Poisson distribution causes serious fluctuation in the device
functions. In addition, relative increase in the influence of solid surfaces and mass transport deteriorate the reliability of devices. One of the methods to fabricate nm structures in a practical way in terms of throughput, process time, and cost is to combine modification of solid surfaces with energetic particles (especially with single ions) and the subsequent chemical processing in solutions.

Since the discovery of SiO$_2$-based bioglass by Hench et al. in 1969 [25], many attempts have been made to explore the possibility of silicon-based materials applied in biological fields [26-30]. Silicon by itself was generally considered to be nonessential in biochemistry, except in certain primitive organisms like diatoms [31]. However, in the past thirty years, silicon has gradually been recognized as an essential trace element in the normal metabolism of higher animals. Carlisle et al. have shown that silicon is required in bone, cartilage and connective tissue formation as well as several other important metabolic processes [32]. Some researchers have confirmed that silicon is involved in an early stage of bone formation. Hidebrant et al. [33, 34] have used modern genetic engineering techniques to demonstrate that certain genes are activated by hydrated silicon. Hydrated soluble silicon will enhance the proliferation of bone cells (osteoblasts) and active cellular production of transforming growth factors. Xynos et al. [35] have also shown that the critical concentration of ionic products dissolved from the bioactive glass composed of soluble silicon and calcium ions can enhance osteogenesis through direct control over genes that regulate cell cycle induction and progression. Therefore, an increasing number of silicon-based materials are being studied for applications in biomedical materials and devices.

Hydrogen in silicon has been widely investigated in the semiconductor area. It has been discovered that hydrogen in silicon greatly changes the electrical property of the resultant electronic devices by passivating shallow-level and deep-level defects [36]. It has been further reported that high dose implantation of hydrogen and subsequent annealing induce splitting of Si, which is utilized in the fabrication of silicon on insulator (SOI) materials [37]. The surface hydrogenation of single-crystalline silicon and corresponding biocompatibility has also been reported by Dahmen and his colleagues [21]. Based on our literature search, the application of hydrogenated silicon to improve the bioactivity or bone conductivity of silicon has pretty much been unexplored, but the materials could have exciting implications in biomedical engineering and biosensor technologies because silicon-based devices often suffer from problems associated with interfacing to the biological environment. The concept of utilizing Si itself as a bioactive miniaturizable packaging material might provide a solution to some of these problems.

In this part, by paying special attention to single ion irradiation as a tool to modify solid surfaces in single-crystalline silicon, we first describe the
methods for single-crystalline silicon surface modification and observation of solid surfaces, and then introduce some examples of the application in biomedical fields.

3.1.2. Plasma treated methods

Hydrogen was implanted into the single-crystal <100> wafers polished on one side using plasma immersion ion implantation (PIII) [13]. The background pressure was pumped to 0.6 μTorr and high-purity hydrogen gas was bled into the vacuum chamber to establish a working pressure of 0.5 mTorr. The schematic diagram of plasma ion immersion implantation and relative parameters are listed in Fig.7 and Table I, respectively. Previous results have shown that H⁺ is the dominated ion species in the plasma under these conditions [38].

The surface structure and roughness of hydrogen-implanted silicon was investigated using atomic force microscopy (AFM) and cross-sectional transmission electron microscopy (XTEM) was performed to identify the nature of defects produced by ion implantation. The crystalline quality of the as-implanted samples was assessed using channeling Rutherford Backscattering Spectrometry (c-RBS) with an incident beam of 2 MeV He⁺ at a backscattering angle of 170°. Secondary ion mass spectrometry (SIMS) measurements were carried out using a Cameca IMS-4F with a Cs⁺ primary beam and the intensities of 28Si⁺ and H⁺ ions sputtered from the center of a 150-μm-diameter crater were monitored. The surface biomedical properties are

![Figure 7. Schematic diagram of plasma ion immersion implantation [13].](image-url)
Table I. Implantation Parameters [13].

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Implantation voltage (kV)</td>
<td>30</td>
</tr>
<tr>
<td>Pulse frequency (Hz)</td>
<td>50</td>
</tr>
<tr>
<td>Pulse duration (μs)</td>
<td>500</td>
</tr>
<tr>
<td>RF Discharge power (W)</td>
<td>1400</td>
</tr>
<tr>
<td>Implantation time (mins)</td>
<td>20</td>
</tr>
<tr>
<td>Implantation dose (cm⁻²)</td>
<td>~1.4 x 10¹⁷</td>
</tr>
</tbody>
</table>

Table II. Ion concentration of SBF in comparison with human blood plasma [39].

<table>
<thead>
<tr>
<th>Ion</th>
<th>Concentration (mM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na⁺</td>
<td>142.0</td>
</tr>
<tr>
<td>K⁺</td>
<td>5.0</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>2.5</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>1.5</td>
</tr>
<tr>
<td>HCO₃⁻</td>
<td>4.2</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>148.5</td>
</tr>
<tr>
<td>HPO₄²⁻</td>
<td>1.0</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>0.5</td>
</tr>
</tbody>
</table>

characterized via soaking in a simulated body fluid (SBF) for some days and the ionic concentrations in the solution are nearly equal to those in human body blood plasma, as shown in Table II [39].

3.1.3. Surface activation

The surface images of the hydrogen implanted single-crystal silicon displayed in Fig. 8. The surface of the hydrogen implanted silicon is quite smooth with a root mean square (RMS) roughness of about 0.235 nm which is closed to the roughness of the silicon wafer before hydrogen implantation. The cross-section TEM micrograph of the hydrogen implanted silicon wafer in Fig. 9 reveals the formation of defects. There exists a top amorphous zone (about 60 nm in thickness) and a dense dislocation zone (about 150 nm). The dense dislocation zone is located around the projected range of H₃⁺. Fig. 10 plots the atomic dislocation density versus depth derived from c-RBS and the hydrogen elemental depth profile acquired by SIMS. Hydrogen is mainly found on the near surface to about 170 nm (~ 8 at. %) which is the projected range of H₃⁺ obtained from the SRIM code. A total atomic displacement zone (amorphous silicon a-Si) is extended from the top surface to the depth of about 50 nm (slightly different from the TEM results due to calibration and instrumentation issues) followed by a dislocation zone located close to the projected range of H₃⁺. Hence, the implanted sample consists of a highly hydrogen-doped surface with high crystalline disorder.
Figure 8. The surface images of the hydrogen implanted single-crystal silicon [39].

Figure 9. Cross-section TEM micrograph of the hydrogen implanted silicon wafer.

Figures 11 and 12 depict the surface views of the un-implanted and hydrogen-implanted samples of the single-crystal silicon after soaking in a simulated body fluid (SBF) for 14 and 28 days. After 14 days immersion in the SBF, the surface of un-implanted silicon remains smooth similar to that of a silicon before immersion (Fig. 11a), while some single and clustered ball-like particles are observed on the surface of the hydrogen-implanted silicon surface (Fig. 12a). The surface of silicon is, however, not covered completely. After an
Figure 10. The atomic dislocation density versus depth derived from c-RBS and the hydrogen elemental depth profile acquired by SIMS.

Figure 11. The surface views of the un-implanted samples of the single-crystal silicon after soaking in a simulated body fluid (SBF) for: (a) 14 days, (b) 28 days. The immersion time of 28 days, the number of these ball-like particles increases and the surface is totally covered by the newly formed layer (Fig. 12b). In contrast, no new substance can be found on the surface of the un-implanted silicon even after soaking in SBF for 28 days (Fig. 11b).

Calcium and phosphorus cannot be detected on the surface of the un-implanted silicon after soaking for 14 and 28 days (Fig. 13(a) and (b)) indicating
Surface modification of Si-based materials by plasma gas treatments

Figure 12. Surface views of hydrogen implanted silicon wafer soaked in SBF for: (a) 14 days, (b) 28 days.

Figure 13. (a) and (b) no Ca-P layer has formed on the surface of un-implanted silicon.

that no Ca-P layer has formed on the surface. On the other hand, the XRF spectra acquired from the hydrogen-implanted silicon soaked in SBF for 14 days show the existence of calcium and phosphorus on the surface (Fig. 14a). After immersion in SBF for 28 days, more calcium and phosphorus are detected indicating the formation of a denser and thicker Ca-P layer (Fig. 14b). The atomic ratios of Ca to P calculated from the XRF spectra of the hydrogen-implanted silicon soaked in SBF for 14 and 28 days are about 1.33 and 1.58, respectively.

These results show that the atomic ratio of Ca to P in the Ca-P layer increases gradually to that of hydroxyapatite (1.67) with longer immersion time in SBF. This means that the Ca-P layer formed on the surface of the hydrogen-implanted silicon can crystallize to form hydroxyapatite with increasing
immersion time in SBF based on the supporting XRD results that will be discussed as follows. Only crystalline silicon peaks are observed while no crystalline apatite peaks appear in the XRD patterns of the un-implanted silicon soaked in SBF for 14 days and 28 days (Fig. 15 (a)). Compared with the XRD pattern of the hydrogen-implanted silicon wafer before immersion, the XRD pattern of the hydrogen-implanted silicon soaked in SBF for 14 days reveals obvious changes. One silicon peak disappears as shown in Fig. 15 (b), but the newly formed Ca-P layer cannot yet be identified unambiguously. The reason for this is believed to be that the Ca-P layer is not yet crystallized to
Figure 16. The broad OH\(^{+}\) absorption bands from 3700 to 2500 cm\(^{-1}\) and weak water absorption band around 1650 cm\(^{-1}\).

form apatite and the amorphous structure still exists. After an immersion time of 28 days, the peaks of crystalline apatite can be easily identified in the XRD spectra indicating the formation of a new surface layer composed of crystalline apatite. The broadening of the peaks suggests that the apatite particles formed on the hydrogen implanted silicon are superfine or have low crystallinity [39].

The broad OH\(^{+}\) absorption bands from 3700 to 2500 cm\(^{-1}\) and weak water absorption band around 1650 cm\(^{-1}\) can be seen in FTIR spectra (Fig.16). Bands between 1400 and 1550 cm\(^{-1}\) are due to the carbonate IR absorption \(\nu_3\). The peak around 870 cm\(^{-1}\) arises from the both the carbonate and HPO\(_4^{2-}\) ions [40]. The broad bands around 1100 cm\(^{-1}\) are mainly attributed to the phosphate. According to Canham and co-workers [30], a sharp P-O bending mode doublet around 600 cm\(^{-1}\) is indicative of a crystalline phase of hydroxyapatite being present. In Fig. 9, the double peak around 600 cm\(^{-1}\) in the FTIR spectra of the hydrogen-implanted silicon soaked in SBF for 28 days is clearer than that in the hydrogen-implanted silicon soaked in SBF for 14 days. These mean that carbonate-containing hydroxyapatite (bone-like apatite) forms on the surface of the hydrogen-implanted silicon wafer soaked in SBF, indicating that the hydrogen-implanted single-crystal silicon has good bioactivity.

3.1.4. Analysis of surface activation

Hydrogen is implanted into single-crystal silicon wafers using plasma ion immersion implantation to improve the surface bioactivity and recent results
reveal the presence of a disordered silicon surface containing Si-H bonds after hydrogen implantation. When the sample is immersed in a simulated body fluid, the Si-H bonds on the silicon wafer initially react with water to produce a negatively charged surface containing the functional group (=Si-O') that subsequently induces the formation of apatite. A good understanding of the formation mechanism of apatite on hydrogen implanted silicon is not only important from the viewpoint of biophysics but also vital to the actual use of silicon-based microchips and MEMS inside a human body.

In the past three decades, silicon has gradually been recognized to be an essential trace element in the normal metabolism of higher animals, and the role of silicon in the human body has aroused interest in the biomedical community [32]. An increasing number of silicon-containing materials is being investigated as potential materials in biomedical devices and medical implants. Silicon-based microelectronics and biosensors have undergone tremendous technical development but the bioactivity and biocompatibility of silicon is relatively not well understood. In fact, the surface biocompatibility of silicon is usually poor and the interaction between silicon-based biosensors or MEMS and the human body may not be desirable [41]. Long-term problems associated with the packaging and biocompatibility of Si chips have thus been identified to be a major issue [42]. Some attempts have been made to improve the bioactivity and biocompatibility of silicon wafers. Dahmen and co-workers have shown that surface functionalization of amorphous hydrogenated silicon (a-Si:H) and amorphous silicon suboxide films (a-SiO_x:H) produced by a hydrosilylation reaction are largely biocompatible [14]. The role of hydrogen in silicon has been under intense investigation as it is known to passivate defects, deactivate dopants, and sometimes induce point or extended defects. In contrast, the use of hydrogenation to improve the surface bioactivity of silicon has pretty much been unexplored. What is the direct proof that the bioactivity of silicon by hydrogen plasma immersion ion implantation (PIII)?

It is well known that the surface plays an important role in the response of the biological environment of the artificial biomedical devices. Therefore, it is logical to believe that the improvement of the bioactivity of the implanted silicon results from the modified surface by hydrogen implantation. The experimental results from TEM, RBS and SIMS reveal the presence of an amorphous hydrogenated silicon layer (a-Si:H) after hydrogen PIII. In order to investigate clearly the formation mechanism of bone-like apatite on the surface of the hydrogen implanted silicon, two comparative experiments were also conducted. One is to investigate the bioactivity of hydrogenated silicon with no surface damage and the other one is to evaluate the bioactivity of argon implanted silicon which possesses an amorphous surface but no hydrogen. After the hydrogenated silicon wafer and argon implanted wafer are
soaked in SBF for 28 days, no apatite particles can be found on either surface, indicating poor bioactivity on both samples. These suggest that only the formation of an amorphous hydrogenated silicon (a-Si:H) surface can improve the bioactivity of silicon and results in the formation of bone-like apatite on its surface after treatment in SBF. Experimental evidence indicates that the formation of apatite requires that the surface be both amorphous and be hydrogenated. The detailed mechanism can be described as follows:

Hydrogen is known to interact with silicon in a wide variety of ways, including passivating the surface, deactivating dopants, and passivating shallow as well as deep levels. In the H-PIII silicon wafer, many dangling bonds are produced [43], and the surface of the silicon wafer exhibits an amorphous network with disorders and defects. In the H-PIII silicon wafer, hydrogen passivates dangling bonds by forming Si-H bonds. When the H-PIII silicon wafer is soaked in the SBF solution, the following reactions are believed to occur. The \( \equiv \text{Si-H} \) structure is first hydrated to form silanol (\( \equiv \text{Si-OH} \)) by the following reactions:

\[
\equiv \text{Si-H} + \text{H}_2\text{O} \rightarrow \equiv \text{Si-OH} + \text{H}_2.
\]

Afterwards, the silanol (\( \equiv \text{Si-OH} \)) reacts with the hydroxyl ion to produce a negatively charged surface with the functional group (\( \equiv \text{Si-O}^- \)) as follows:

\[
\equiv \text{Si-OH} + \text{OH}^- \rightarrow \equiv \text{Si-O}^- + \text{H}_2\text{O}.
\]

The formation of negatively-charged surface on bioceramics and bioglasses is generally regarded to be important to the precipitation of apatite. Li, et al. have applied a \('\text{charged surface}'\) theory to explain the reaction of bioactive glass in simulated physiological solution and it is believed that precipitation of apatite on the surface of the bioactive glass soaked in SBF is due to the formation of an electric double layer in the glass-solution system. Takadama, et al. investigated the mechanism of bio-mineralization of apatite on sodium silicate glass using TEM-EDX and also proposed that the formation of apatite on the surface of sodium silicate glass was mainly attributed to the charge surface [44-46]. Due to the formation of the negatively-charged surface, the calcium ions in the SBF solution are attracted to the negative charged surface site of the silicon wafer. This is followed by the arrival of \( \text{HPO}_4^{2-} \) resulting in a hydrated precursor cluster consisting of calcium hydrogen phosphate. After the precursor clusters are formed, they spontaneously grow by consuming calcium and phosphate ions from the surrounding body fluid. The calcium phosphate phase that accumulates on the surface of the silicon wafer is initially amorphous. It later crystallizes to a carbonate-containing
hydroxyapatite (CHA) structure by incorporating carbonate anions from the solution within the amorphous calcium phosphate phase.

Generally, all cells are enclosed by a layer of hydrated biopolymer. Thus, the adherent properties of cells to an ideal solid planar substrate can be deduced partly from the water contact angle [47]. A hydrophilic surface is suitable for the adhesion and spreading of cells. Therefore, the surface of the H-Pill silicon wafer is favorable to the adhesion and growth of osteoblast cells. However, it should be noted that cell adherence is also affected by many other biological interactions, and some of them may overwhelm the effects of hydrophilicity.

3.2. Amorphous silicon (a-Si:H)
3.2.1. Background
The research in the field of amorphous semiconductors, from the very beginning, has been driven by both the scientific interest in basic aspects of disorder in the properties of solids and technological applications. In the early years, chalcogenide glasses were at the center of the interest owing to thin-film applications in imaging, xerography, memory and switching devices. At that time, amorphous silicon and amorphous germanium, a-Si and a-Ge, were of more academic scientific interest [48, 49]. As simple elemental tetrahedrally bonded amorphous semiconductors, they served as model systems in which the disorder was less complicated, being defined not chemical composition but by the structural disorder only. These amorphous semiconductors were prepared as thin films, about 0.1-1 micro meter thick, on glass or quartz substrates by a variety of methods such as thermal or e-gun evaporation, sputtering, ion bombardment and electrolysis. The simplest model for the structure of tetrahedrally bonded semiconductors is the continuous random network (CRN) structure in which the average coordination number is close to 4. Fluctuations in the bond angles and nearest-neighbor distances lead to a loss of long-range order even in the second-neighbor shell. This loss of long-range order is the characteristic structural feature of amorphous semiconductors. As a result, important theoretical concepts which are based on periodicity (Bloch's principle) fail, such as band structure, k-vector, Bloch states, effective masses and optical selection rules [50]. The optical spectra of amorphous semiconductors appear to be more or less broadened versions of their crystalline counterparts, which show that the density-of-states distribution is the decisive quantity; this is largely determined by the nature and structure of the chemical bonding. Perhaps the most obvious effect of disorder is the localization of electronic states; in particular near the band edges, which strongly affect the transport properties.

In the 1960s, the major challenge consisted in understanding the role of disorder and in developing new theoretical concepts. However, the early forms
of amorphous silicon had unacceptable electronic properties due to large defect densities, which caused high densities of states in the energy gap, which pinned the Fermi level. The only defect that has been identified microscopically by electron spin resonance is the Si dangling bond (Si-db), which is present in an amount of some $10^{19}$ cm$^3$ in evaporated or sputtered material. Si dangling bonds form deep gap states, which act as effective centers for nonradiative recombination. The conductivity in this kind of amorphous silicon was very low and, below room temperature, was in general determined by hopping transport between localized gap states. Owing to the effective pinning of the Fermi level in a high density of gap states, the conductivity could not be varied by doping, illumination or carrier injection. Such material properties prevented this material from being useful for electronic devices [51].

The situation changed rather abruptly when the beneficial role of hydrogen incorporation was discovered at the beginning of the 1970s. Six main milestones in the material and device research led to a burst of research activities in this field and to numerous applications of hydrogenated amorphous silicon, (a-Si:H).

The first to use the plasma deposition technique were Chittick, Alexander and Sterling in 1969. In this technique, silane was decomposed in a radio-frequency (RF) glow discharge and the film was formed on heated substrates [49].

The work at the University of Dundee showed that the defect density in this kind of amorphous silicon was below, which resulted in high photoconductivity. The essential role of hydrogen in passivating defects was first discovered by the Harvard group, studying sputtered a-Si:H and a-Ge:H. Later on, numerous studies gave proof that the superior semiconducting and photoelectric properties of glow-discharge-deposited amorphous silicon were due to the incorporation of hydrogen.

In 1975, Spear and LeComber reported on substitutional n-type and p-type doping by addition of phosphine or diborane to the process gas. This procedure allowed one to control the electrical conductivity over 10 orders of magnitude [51].

The first report on photovoltaic devices, by Carlson and Wronski in 1976, demonstrated the feasibility of a-Si:H solar cells [52].

The research on displays started some years later, after the first report on the fabrication and physics of a thin-film transistor (TFT) [53, 54].

The preparation and properties of plasma hydrogenated amorphous silicon have been described in numerous review articles and monographs and the development is well documented in the proceedings of the biannual International Conference on Amorphous and Microcrystalline Semiconductors, which are published in regular issues of the Journal of Non-Crystalline Solids.
Today hydrogenated amorphous silicon, a-Si:H, offers a mature material and device technology, used for solar cell, thin-film transistors, sensors, imaging, radiation detectors and displays. Among the various material choices for thin-film solar cells, this is the only technology which so far has been able to overcome the barrier to mass production of large-area modules and to occupy a reasonable share of the world market (about 10%).

3.2.2. Experimental methods

Amorphous silicon cannot be made by rapid cooling of a Si melt. The amorphous material, instead, is prepared by deposition from the gas phase onto substrates which are held at temperatures far below the melting temperature. A large variety of techniques has been used: thermal evaporation, sputtering, chemical vapor deposition using silane (CVD), photo-CVD, plasma-enhanced chemical vapor deposition (PECVD), and thermo-catalytic how-wire deposition (HWCVD). There are no differences in principle in the microstructures of amorphous films prepared by the various methods. The differences lie in the deposition rate and the kind and concentration of defects (dangling bonds and voids). PECVD has led to the lowest defect densities and, therefore, is widely used now in industrial applications.

Thermodynamically, amorphous silicon (a-Si) is in a metastable state. Although an ideal structure might be described by a random network structure, the real structure can be varied experimentally in many ways. Therefore the material properties strongly depend on the preparation conditions and on the thermal history of an amorphous sample. Thermal annealing has been shown to produce changes in practically all material properties (enthalpy, electrical properties, defect densities, optical properties, etc.). It has been found that the free energy of annealed a-Si (relaxed states) is about 0.11 eV/atom higher than that of crystalline silicon. Heating above a temperature of above 500°C usually induces a transition into the thermodynamically more stable crystalline phase. The kinetics of solid phase crystallization (SPC) is characterized by nucleation and growth of crystal clusters at the expense of the surrounding amorphous material. Laser recrystallization of amorphous silicon has become an important technique for the fabrication of polycrystalline silicon thin-film transistors. Recently, SPC has attracted high interest as a result of the experience that the presence of certain metals strongly modifies the nucleation and the growth process. Such techniques enable the engineering of polycrystalline silicon thin films at low temperatures for new device application such as thin-film transistors or polycrystalline silicon thin-film solar cells. A particularly interesting example of this kind of processing is the creation of a polycrystalline silicon layer with a grain size of about 10 μm on a glass substrate by an Al-induced layer exchange process. In this process, a film
Surface modification of Si-based materials by plasma gas treatments

The stack of glass/Al/a-Si is transformed by annealing at about 400°C into glass/pily-Si/Al(Si) such that after etching of the Al(Si) layer a polycrystalline silicon layer on glass remains, which may serve as a seeding layer in subsequent deposition process.

In PECVD, silane or mixtures of silane with rare gases or hydrogen are decomposed in a glow discharge. In most cases, parallel-plate systems in a stainless steel reactor have been used. The most important deposition parameters are substrate temperature, base pressure, and flow rate of the process gas, power density and frequency. High-quality a-Si:H films are grown at deposition rates of typically 0.1 nm/s at substrate temperatures in the range 150-250 °C. The progress achieved by using this method is that the density of deep defects (Si dangling bonds) can be reduced to values of below $10^{16}$ cm$^{-3}$ owing to the incorporation of hydrogen. The effect of hydrogen is to saturate dangling-bond defects and to lower the average coordination number, which allows the construction of a more relaxed disordered network. The hydrogen content can vary widely with the deposition conditions (5-40%). Infrared spectroscopy reveals various bonding configurations of hydrogen. In optimized films, the hydrogen concentration amounts to 5-15% and the density of neutral Si dangling bonds is less than $10^{16}$ cm$^{-3}$. The IR spectra of such films show that the hydrogen is bonded predominantly in an isolated Si-H configuration (absorption at 2000 cm$^{-1}$). However, NMR studies suggest that the hydrogen may be inhomogeneously distributed. Annealing of the films at temperatures above the deposition temperature leads to the evolution of hydrogen, which is accompanied by an enhancement of the defect density. In films deposited at around 250°C, the evolution rate peaks at 550°C, whereas films made at lower temperatures tend to show a second evolution peak near 350°C. The occurrence of this low-temperature peak points to the existence of a porous structure, which enables rapid hydrogen diffusion. Owing to the pronounced role of hydrogen, this kind of amorphous silicon may be considered rather as a hydrogen-silicon alloy. Practically all film properties depend on the hydrogen content.

A particular advantage of plasma deposition is a high flexibility in the choice of the process gases, which allows one to easily modify the properties of the deposited films. Variations of the deposition parameters have been found to result in higher deposition rates and modifications of the material. Doping can be achieved by adding controlled amounts of B$_2$H$_6$ or PH$_3$ to the process gas. Alloy films such as a-Si$_{1-x}$Ge$_x$:H and a-Si$_{1-x}$C$_x$:H can be deposited from gas mixture of SiH$_4$ with GeH$_4$ or CH$_4$, respectively. These films allow one to tune the energy gap to lower or higher values by controlling the composition of the process gas. Strong hydrogen dilution of the process gas results in the formation of microcrystalline silicon films ($\mu$-Si:H). The
structural and electronic properties of such plasma-deposited films have been studied intensively over more than 20 years.

3.2.3. Electronic properties

The electronic properties of the amorphous films depend sensitively on the density and energy distribution $N(E)$ of the localized gap states. In particular, these states determine the shape of the absorption edge, the doping efficiency, transport and recombination, as well as the widths of space charge layers in devices. Fig. 17 displays the density of localized states, $N(E)$, plotted against the energy $E_g - E$ for a number of a-Si samples produced using the 'glow discharge' (or PECVD) technique in SiH$_4$ gas, including both intrinsic and extrinsic defect states [55]. Inside the bands, the density-of-states (DOS) distributions of the valence and conduction bands of amorphous semiconductors differ only little from those of their crystalline counterparts. In the optical spectra, the main effect is a broadening of the spectra. The states inside the bands are considered to be delocalized but, of course, owing to the loss of long-range order, they are no longer Bloch states. An important effect of disorder is that closer to the band edges, the states become localized. The most widely applied model suggests that a transition from extended to localized

Figure 17. The density of localized states, $N(E)$, plotted against the energy $E_g - E$ for a number of a-Si samples produced using the 'glow discharge' (or PECVD) technique in SiH$_4$ gas. The temperature $T_d$ refers to the deposition temperature. $E_g$ refers to an evaporated Si sample. $L$ and $S$ denote linear and square law interpolations, respectively [55].
states occurs at distinct energies $E_C$ and $E_V$, where the carrier motilities drop abruptly owing to the change in the character of the states. In an amorphous semiconductor, these mobility edges play a similar role to the band edges in crystalline materials.

A characteristic of the DOS distribution in amorphous semiconductors is tails of localized extending from both edges deep into the gap. These states are considered to arise from potential fluctuations due to disorder. In addition to these tail states, one expects deep states which originate from specific defects. Such defects may be formed in a random network structure in order to release internal stress but may also arise from unfavorable growth conditions. In a-Si:H, the simplest deep defect is an unsaturated bond (Si-db), which has three differently charged states: unoccupied (positive, $D^+$), singly occupied (neutral, $D^0$) and doubly occupied (negative, $D^-$). In undoped a-Si:H, the $D^0$ state is located around midgap, while the $D^-$ state is higher in energy by the correlation energy of about 0.2 eV. Extrinsic states originate from impurities. These films contain hydrogen in a concentration of up to 15 at% and are strongly contaminated with oxygen, nitrogen and carbon in concentration of the order of $10^{19}$ cm$^{-3}$. So far no gap states due to these impurities have been identified. The only known impurity states are those that arise from substitutional doping by incorporation of elements from group III and V of the periodic table, forming flat donor or acceptor states.

The shape of the absorption edge reveals the general features of the DOS distribution. A comparison of the absorption spectra of amorphous and crystalline silicon reveals a shift of the absorption edge of a-Si:H to higher energy and a strong enhancement of a absorption in the visible range of the spectrum, which has often been related to the relaxation of the $k$-selection rule due to the loss of long-range order. This enhancement of absorption is the basis of important applications such as solar cells, and imaging and optical sensors. An optical gap may be defined in different ways. Rather often, $E_{03}$ and $E_{04}$ are used, which are the photon energies where $\alpha=10^3$cm$^{-1}$ and $10^4$cm$^{-1}$, respectively. Another, more physical way is to use the concept of nondirect optical transitions, which takes into account the loss of the $k$-selection rule in a disordered structure by plotting the data as $(\alpha h\nu)^{1/2}$ versus $h\nu$ (Tauc plot). By extrapolating the straight line to the energy axis, values for the energy gap of about 1.75 eV are found. A justification for this procedure is that similar values have been obtained from the analysis of transport properties. However, one has to keep in mind that in this case the analysis yield a different quantity, namely the value of the mobility gap $E_C - E_V$. The value of the energy gap appears to be a unique function of the hydrogen concentration $C_H$ in the film. It amounts to 1.2-1.5 eV in evaporated or sputtered material with $C_H=0$ and increases linearly with $C_H$ in hydrogenated films (1.6-2.0 eV) [56].
Below $\alpha = 3 \times 10^3 \text{ cm}^{-1}$, the absorption constant decreases exponentially with energy; $\alpha \sim \exp[-(E/E_0)]$ (Urbach edge). The Urbach parameter $E_0$ depends on both temperature and the general disorder in the film. The Urbach edge can be related to the exponential bandtails, and it is commonly believed that in a-Si:H the slope of the absorption edge is determined by the slope of the valence bandtail. The values of $E_0$ (50 meV) for films prepared under optimized conditions agree fairly well with the slope of the exponentially varying density of states of the valence bandtail derived from transport studies. The conduction bandtail is considerably steeper. Time-of-flight experiments have been consistently explained by a slope of about 25 meV.

At low photon energies, the absorption curve of a-Si:H levels off and a plateau develops, which is assigned to defect absorption. This defect-related absorption shoulder at low photon energies has quite frequently been used for quantitative defect analysis, applying techniques such as photocurrent spectroscopy and photothermal spectroscopy. The value of $\alpha$ in this energy range is considered a figure of merit for the film quality. In undoped optimized films where, according to electron spin resonance, the concentration of neutral dangling bonds is about $10^{16} \text{ cm}^{-3}$, the value of $\alpha$ at 1.25 eV is in the order of $1 \text{ cm}^{-1}$.

The transport properties are strongly affected by disorder. In a-Si:H, where the density of gap states is low, transport is considered to take place predominantly in extended states above the mobility edges $E_c$ and $E_v$. The carrier mobility cannot be determined experimentally as in crystalline silicon by the Hall Effect, owing to the sign anomaly in amorphous semiconductors. The observation, the explanation of which is still one of the challenges in this research field, is that the sign of the Hall Effect is opposite to that expected for the predominant carriers, that is, positive for electrons. It is estimated that the mobility of the extended states is in the region of $10 \text{ cm}^2/\text{Vs}$. Carriers in localized states can contribute to conduction with much lower mobility by thermally activated tunneling (hopping transport). If the density of states at the Fermi level is high, variable-range hopping may be observed, with a characteristic temperature dependence of the conductivity, $\ln \sigma \sim -(T_0/T)^{1/4}$. The existence of sharp mobility edges is still controversial and has been questioned as a result of consideration of electron-photon coupling. Although there is no direct proof for their existence, most experimental results are discussed in terms of this model [57].

A breakthrough in the physics of amorphous semiconductors was the discovery that a-Si:H can be effectively doped by adding controlled amounts of PH$_3$ or B$_2$H$_6$ to the process gas. In an amorphous semiconductor, the donors deliver their electrons to empty states near the Fermi level. The resultant shift of the Fermi level, therefore, depends on the DOS distribution, and the doping
Surface modification of Si-based materials by plasma gas treatments

Effect in a-Si:H is closely related to the low density of defect states. For P doping, the maximum conductivity at 300 K, $\sigma_{RT}$, of about $10^{-2}$ S cm$^{-1}$, is attained at a concentration of $10^3$-10$^4$ ppm PH$_3$ in the gas phase. At higher doping levels, $\sigma_{RT}$ decreases, presumably owing to the generation of additional defects. For B doping, $\sigma_{RT}$ decreases at low doping levels, and attains a high doping level a maximum close to $10^{-3}$ S cm$^{-1}$. At the minimum, the Fermi level crosses midgap, $E_c-E_F=(1/2)(E_c-E_V)$, and the type of conduction changes from n- to p-type. Using $\sigma_{RT}=10^{-12}$ S cm$^{-1}$, the value of the mobility gap can be estimated as 1.7 eV at 300 K. Whereas at high doping levels the results from different laboratories agree fairly well, there are pronounced differences at low doping levels. This is an expression of the influence of the specific deposition conditions on the concentration of deep defects. The details of the doping mechanism have turned out to be very complicated, involving reactions with dangling bonds and hydrogen. Experiments show that the concentration of defects increases strongly with doping, and both the density and the energy position of the defect states are essentially controlled by the position of the Fermi level. It points to a very general defect creation mechanism.

3.2.4. Biomedical properties

Plasma hydrogenated amorphous silicon (a-Si:H) materials are used in a myriad of applications such as active matrix displays, digital photography, sensors, and solar cells and there are potential applications in biosensors and biomedical micro-devices. In the old days, amorphous silicon films were made without hydrogen by sputtering or thermal evaporation and the materials typically possess a very high defect density which makes doping difficult and exhibit poor photoconductivity and other undesirable characteristics to be a useful semiconductor. The incorporation of hydrogen into amorphous silicon can eliminate many of these defects giving rise to improved materials properties such as photoconductivity [57]. In biomedical engineering, silicon-based materials have gradually gained more attention as biomedical materials. For instance, silicon has been recognized as an essential trace element in the normal metabolism of higher animals [31]. E. M. Carlisle has shown that silicon is required in bone, cartilage and connective tissue formation as well as several other important metabolic processes [32]. The biomedical properties of hydrogenated amorphous silicon (a-Si:H) films have been investigated recently and found that the formation of the Si-H bonds on the surface of silicon wafer was postulated to lead to the improvement in the bioactivity.

A promising method was used to improve the surface bioactivity of silicon via the formation of a hydrogenated amorphous silicon (a-Si:H) layer using PECVD which is a standard technique in thin film fabrication and semiconductor processing. The formation of a thicker modified layer or coating
may bode well for biomedical applications. In the Raman spectra (400–1500 cm\(^{-1}\)) obtained from the a-Si:H film (Fig. 18), the asymmetry peak around 520 cm\(^{-1}\) indicates that the film is disordered. There is also evidence that the deposited film is amorphous that is confirmed by TEM (Fig. 19). The Si-H peak around 2000 cm\(^{-1}\) can be discerned in the higher resolution Raman spectrum. The excellent interface between the silicon wafer and a-Si:H film is
also shown in the high resolution image. The plan view of the a-Si:H films soaked in a simulated body fluid after 14 and 28 days is depicted in Fig. 3. After 14 days, some single and clustered ball-like particles can be observed on the surface (Fig. 19(a)). After 28 days, the number of these ball-like particles increases and the surface is totally covered by the newly formed layer (Fig. 19(b)). Soaking for 14 days leads to the existence of calcium and phosphorus on the surface as shown in Fig. 20(a). After immersion for 28 days, more calcium and phosphorus are detected indicating the formation of a denser and thicker Ca-P layer (Fig. 20(b)). The higher magnification micrograph indicates that the ball-like particles have a coral-like structure composed of many sheet-like crystallites (Fig. 20(c)). The atomic ratios of Ca to P calculated from the XRF spectra are about 1.46 and 1.54 for 14 and 28 days of SBF immersion, respectively (Fig. 21(a) and (b)). It means that the atomic ratio of Ca to P in the Ca-P layer increases gradually to that of hydroxyapatite (1.67) with longer immersion time. This indicates that the Ca-P layer formed on the surface of the a-Si:H film can crystallize to form hydroxyapatite with increasing soaking time. The XRD patterns reveal that the crystalline apatite peaks can be easily identified indicating the formation of a new surface layer composed of crystalline

![Figure 20. Plan view of the silicon wafer with hydrogenated amorphous silicon film after immersion in SBF for (a) 14 days and (b) 28 days; (c) higher magnification of (b).](image-url)
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Figure 21. XRF spectra of the silicon wafer with hydrogenated amorphous silicon film soaked in SBF for (a) 14 days and (b) 28 days.

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<td>CaK</td>
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Figure 22. XRD patterns of the silicon wafer with hydrogenated amorphous silicon film soaked in SBF for 14 and 28 days.

apatite (Fig. 22). Besides, the broad band around 1100 cm⁻¹ in FTIR spectra is mainly attributed to the phosphate [40] (Fig. 23). The carbonate-containing hydroxyapatite (bone-like apatite) can form on the surface of the a-Si:H films after SBF immersion.

It means that the hydrogenated amorphous silicon (a-Si:H) film can induce the formation of bone-like apatite during immersion in SBF and that the
plasma hydrogenation can improve the surface bioactivity of a-Si films. The amorphous surface structure and existence of Si-H bonds are believed to favor the formation of apatite. In fact, the formation of apatite on the hydrogenated amorphous silicon (a-Si:H) can have a similar mechanism to that of the plasma hydrogenation of single-crystal silicon as described accordingly.

All in all, although a-Si:H appears to be a mature technology, it is an incredible testament to the versatility of this basic material that new applications continue to emerge such as memory devices, thermal imaging using filters, spatial light modulators, solar to hydrogen conversion, etc. Where can the a-Si technology make a large impact in the future? A major application on the horizon could be flexible displays: the use of low temperature (~150 °C) during processing and the ability to manipulate the growth etc. allows the use of a TFT on low cost flexible plastic materials, such as PEN and PET. Professor Arokia Nathan’s group have already reported a TFT deposited on plastic substrate at 150 °C with $I_{on}/I_{off} > 10^7$ [53]. They have also reported on nano-crystalline Si NMOS and PMOS structures with field effect mobility of electrons and holes of ~200 and ~35 (cm² s⁻¹ V⁻¹), respectively [54]. The flexible display application represents another multi-billion dollar application, although competition may come from organic semiconductors. Given the history of a-Si and the amount of investments made, a-Si TFTs for this application may prove to be the winner.

Another major application area is in the field of renewable energy, i.e. solar cells or photovoltaics (PV). Renewable energy benefits are not only
obvious but represent a trillion dollar business potential and could dwarf anything in the electronics area. The market for PV in 2004 was ~1300 MW at <$2.50/W and it is expanding at a rate of 20–30% per year. Crystalline Si/multi-crystalline Si solar cells presently dominate the market with thin film Si share at <10%. At the moment, a-Si is represented primarily in niche markets (calculators, battery chargers, applications in building integrated PV etc.). The efficiency of a-Si based commercial modules is <7% (with cost > crystalline Si solar cell) and production levels somewhat insignificant in relation to its crystalline counterpart. There are numerous issues associated with this state of affairs such as, low deposition rate, low gas utilization, use of prohibitively expensive gases such as GeH₄, use of complex current constraining two terminal tandem junctions (instead of perhaps 4-terminal devices [55]) which do not entirely mitigate against the inherent degradation of a-Si. The challenge for thin film silicon to truly realize its potential is to break out of this straight jacket otherwise it may remain marginalized in the rapidly expanding PV market.

3.3. Porous silicon

3.3.1. Background

The scientific field of low dimensional semiconductor structures is a burgeoning and fascinating area of materials science and one that has significant technological implications. The current world-wide interest in porous Si resulted primarily from the proposal in 1990 that efficient visible light emission from high porosity structures arises from quantum confinement effects [58]. This is particularly intriguing for three reasons. First, because porous Si is a Si structure and bulk Si is spectacularly inefficient at emitting light, even at cryogenic temperatures. Second, because the light emitting nanostructure can be "made in a bucket" within minutes, without resort to either the costly lithographic or epitaxial techniques that were at the time, the conventional approaches to realize exceeding small structures. Third, because Si is the most technologically important material known to mankind, and dominates the microelectronics revolution that influences our everyday lives. Light-emitting Si devices could eventually result in a new generation of Si chips and extend the functionality of Si technology from microelectronics into optoelectronics. We deal with areas in some detail but the formation of the material, a range of other important properties, e.g., thermal, mechanical, electrical, chemical, and potential applications such as light-emitting diodes (LED) and sensors. Indeed they are in general considered when they bear some relevance to the prime thrust of the review, namely—what do we now know about the structure of porous Si and what is the origin of its visible luminescence?
In fact, porous Si is not a new material, but it is only relatively recently that its true microstructure and surprising properties have come under close scrutiny. Porous Si was first made some 40 years ago by the Uhlirs at Bell Labs, USA [59]. During studies of the electropolishing of Si in HF-based solutions they observed that the surfaces often developed "a matte black, brown or red deposit". The deposits were "tentatively supposed to be a Si suboxide" and for the next decade largely remained an unwanted scientific curiosity. One year after the original work, Fuller and Ditzenberger reported that similar films could develop in HF-HNO₃ solutions without any externally applied electrical bias to the Si [60]. The "anodized" films first received more detailed study by Turner and the chemical "stain" films by Archer [61]. These films were not recognized as being porous Si, let alone a Si nanostructure, for many years. It was Watanabe and co-workers who first reported their porous nature and the ease with which the oxide films. Pioneering Japanese work on utilizing this for dielectric trench isolation of active Si devices followed in the 1970's [62]. However, it was Imai's so-called full isolation by porous oxidized Si FIPOS process developed at NTT Labs, Tokyo, which prompted a significant rise in the perceived potential of the material in the 1980's [63]. A number of approaches to realizing Si-on-insulator (SOI) circuitry were subsequently developed [64]. Nevertheless, before 1990 there were less than 200 papers published on porous Si, spanning a period of 35 years. Figure 24 shows the dramatic effects that the demonstration of tuneable efficient, room temperature light output from the material generated in 1990. Independently, Lehman reported in 1991 that porous Si could exhibit an increased band gap compared with bulk Si and that this property, as well as the formation mechanism itself, involved quantum size effects [65]. Within a year, not only multicolour (from red to green) photoluminescence but also efficient forms of visible electroluminescence had been achieved, generating considerable excitement. The origin of the luminescence, however, quickly became a very controversial topic and a plethora of models emerged, each supported by specific observations of the microstructure of the material and the spectroscopic nature of the light emission process [58, 66].

Porous media in general should also be classified according to the IUPAC guidelines which define ranges of pore size exhibiting characteristic adsorption properties in Table III [58]. In the porous Si literature, the term "microporous" has often been too loosely applied, and bears no resemblance to the strict criteria now universally accepted by workers studying porous carbons, glasses, etc. Of course, as will become clear, part of the problem is that the optoelectronic properties of porous Si are largely determined by skeleton size not pore size. Nevertheless, the form of porosity still largely determines many properties relevant to characterization and material processing. Semiconductor-
inspired new terminology such as "nanoporous" is currently poorly defined but has been invoked, presumably, to indicate a solid skeleton with dimensions small enough to constitute a nanostructure.

3.3.2. Surface treated method

Although as-anodized, luminescent porous Si is hydrogen passivated and contains essentially no oxygen, exposure to ambient air results in progressive modification of the hydride surface and oxidation of the porous matrix. Furthermore, heating of the porous Si to high temperature in a strongly oxidizing ambient, for example, pure oxygen leads to very rapid oxidation of
the structure. Of special interest is the observation by Petrova-Koch et al. and others that the latter oxidized material can still give efficient [67]. The behavior has given important insight into the physical characteristics of the material, in addition to improving the potential for device exploitation. Oxidation of porous Si at high temperature is conveniently carried out by use of rapid thermal oxidation (RTO); involving transient heating in oxygen ambient so that careful control of the potentially rapid surface reaction can be maintained. The structures of samples treated by RTO at 1000°C for 30 s have been examined in detail by Cullis et al. using TEM observations of cross-sections prepared by ion milling, including finishing with very low energy ~50 eV ions to minimize artefactual damage [58]. Electron diffraction patterns from throughout such a porous layer show the strong diffuse rings expected for a matrix composed mainly of oxide. However, as shown in the inset to Fig. 25, relatively weak Si crystal spots are superimposed upon this for most layer depths and the spots are aligned with those given by the underlying Si substrate. To record the diffraction pattern of Fig. 25, the substrate had been aligned with the electron beam incident along the (110) direction and it is clear that spots given by the 10 mm thick layer comprise a pole pattern identical to that of the substrate [68]. Therefore, aligned Si crystal remains in the porous layer after the high temperature oxidation, and its nature is revealed in dark-field images obtained using the 220 diffracted beam.

The image of Fig. 25 demonstrates that this residual Si crystal is in the form of isolated crystallites denoted as bright area dispersed in the oxide. The maximum nanocrystallite size is about 30 nm, although it is clear that a distribution of crystallite sizes down to below 3 nm is present. While interconnectivity between the Si nanostructures has been lost, essentially all observable isolated. The nanocrystallites remain crystallographically aligned with the underlying substrate. This latter observation indicates that, during high temperature oxidation, significant melting of these nanocrystals due to a suggested depression of the melting temperature did not occur for crystallite dimensions down to at least 3 nm, since recrystallization within an amorphous oxide matrix would have been expected to randomize nanocrystal orientations.

The nanocrystallites are present at almost all positions in the 10 mm layer, although their number density is reduced in very near surface regions, while close to the underlying crystal substrate the connectivity of the remaining Si increases. In the particular area shown in Fig. 25, residual holes in the oxide matrix are visible as 10 nm scale dark regions. It is likely that similar nanocrystallite dispersions can be produced by somewhat lower temperature RTO treatments of porous Si if water vapor is introduced into the oxygen ambient.
3.3.3. Surface states

The observed PL from porous Si would originate from a hydrogenated amorphous (a-Si:H) phase created by the anodizing process. a-Si:H is known to possess a PL band in the visible and alloying effects that introduce varying amounts of hydrogen and oxygen into the material could, in principle, provide a possible explanation for the observed tunability of the PL from porous Si. Interest in this model was increased by early structural studies which reported significant amounts of amorphous material in Fig. 26. Figure 26 shows six headings under which the various proposed models can be grouped [58].

In each case, the heading describes the nature of the material proposed as the origin of the luminescence. In the following, the five extrinsic model groups are briefly described and the reasons and evidence that prompted their proposal are summarized. The models are then critically appraised in light of the evidence now at hand. Particular attention is paid to results which are well understood, and clear in their implications for a particular model group. Finally, the status of the quantum-confinement model is discussed, and the ability of this model to explain the wealth of results presently available is assessed.

More recently, some authors have still proposed that the luminescence is associated with highly disordered material. SiH$_2$ surface species were proposed as the luminescent species in porous Si [72, 73]. The PL intensity decreases dramatically if the hydrogen is thermally desorbed from the as anodized porous Si surface and that the PL intensity can be regained with a brief HF etch.
Figure 26. The six groups of models proposed to explain the PL from porous Si. Detailed discussion of these various models are given in Section VII, here the model groups are illustrated pictorially under titles referring to the nature of the luminescent material involved. Part (a) shows a section of an undulating crystalline Si quantum wire. A surface defect renders one undulation nonradiative, whereas an exciton localised in a neighbouring undulation recombines radiatively. Part (b) shows a crystalline Si nanostructure surrounded by a surface layer of hydrogenated amorphous Si. Radiative recombination takes place within the surface amorphous layer. Part (c) shows a hydride passivated Si surface with mono-, di- and tri-hydride termination. Radiative recombination occurs from the Si hydride bonds. Part (d), taken from Ref. 69, shows a partially oxidised Si structure containing various defects which have been proposed as radiative centers in porous Si: the oxygen shallow donor (SD), nonbridging oxygen hole center (NBOHC) and Pb dangling bond. Part (e), taken from Ref. 70, shows the molecular structure of siloxene, a Si-based polymer proposed to exist on the large internal surface of porous Si and to be responsible for the luminescence from this material. Part (f), taken from Ref. 71, shows a Si dot with surface states that localize electrons and holes either separately (upper part of figure) or together (lower part of figure), these carriers subsequently recombine radiatively.

which restores the hydride coverage. This suggestion followed work which had demonstrated the existence of a tuneable visible PL band proposed as due to SiHₓ groups. The hydrogen desorption work has subsequently been restudied and reinterpreted. FTIR studies have shown that the PL is quenched while the majority of the hydrogen still remains on the Si surface. The loss of
the PL intensity as the hydrogen is desorbed correlates more closely with the formation of an efficient nonradiative channel, through the creation of dangling bonds on the now poorly passivated surface of the Si, than with the loss of a luminescent hydride species. Perhaps the most conclusive evidence that surface hydrides are not responsible for the PL is the observation that efficient PL can also be obtained from porous Si where the hydride passivation has been replaced by a high quality oxide formed chemically or thermally. It is, therefore, clear that hydride passivated porous Si is only one of a number of possible luminescent forms of this material. Furthermore, no correlation of the PL intensity with hydride coverage is observed for porous Si samples with different morphologies; macroporous Si can have a large hydride passivated internal surface and yet exhibits no visible PL. Indeed, work has shown that the intensity of the PL from low porosity films can be enhanced by over three orders of magnitude by an anodic oxidation that reduces the dimensions of the Si material while at the same time reducing the hydrogen coverage. In addition, the spectroscopic arguments outlined previously argue strongly against hydride surface species as the origin of the PL.

The very large internal surface area of porous Si has led to proposals that this surface is involved in the emission process. In these models absorption takes place in the quantum confined Si, but the radiative recombination occurs in states localized at the surface of porous Si, or in an interfacial region between the Si and an oxide. Deep surface states that strongly localize carriers have been proposed and so, more recently, have shallow surface states that do not strongly localize carriers. The large energy difference between the absorption and PL peaks in porous Si has been put forward as evidence that photocreated carriers relax into surface states. Spectroscopic evidence is against the attribution of the PL from porous Si to deep surface states. The resonantly excited PL results described previously show clearly that the PL from porous Si arises from excitons which couple to momentum-conserving phonons with momentum equal to the conduction band minimum of crystalline Si. This implies that the wave function of the exciton is spread over many Si atoms, and not localized on an atomic scale as would be the case for excitons localized at deep surface states. If such a strong localization occurred, momentum conservation would completely break down and excitons would couple to phonons with a broad range of momenta, and also to those associated with local vibrational modes of the trapping center. The size of the exchange splitting in porous Si taken from resonantly excited PL spectra and extracted from temperature dependent lifetime measurements also suggests that carriers are not localized on atomic length scales, but rather sample the whole volume of the Si nanostructures they are contained in. Furthermore, the observed polarization of the PL and the fact that this polarization extrapolates linearly to
the bulk Si band gap, rather than tailing off to energies below it, implies that S-
band luminescence does not originate from localized states in the gap, but
rather from bulklike confined states. As mentioned above, shallow surface
states that only weakly localize carriers at the surface of crystalline Si
nanostructure also have been proposed. The properties of these shallower
surface states closely approximate those of pure bulklike states as the degree of
surface localization decreases and this model becomes indistinguishable from
the quantum confinement model. The spectroscopic evidence that exists at
present does not allow discrimination on this fine scale. Future theoretical and
experimental work may be able to determine the degree of surface localization,
if any, of carriers in porous Si [74-76].

3.3.4. Photoluminescent properties
Porous Si has been extensively studied using spectroscopic techniques,
and our understanding of the interesting and unusual optical properties of this
material is now well developed. The upshift and tunability of the PL, its high
quantum efficiency despite a long radiative lifetime and the magnitude and
form of the variation of the PL lifetime and intensity with temperature can all
now be seen as natural consequences of the effects of quantum confinement in
the undulating crystalline Si wires observed to be present in porous Si.
Additionally a number of other observations strongly support the quantum
confinement model, for example the upshift of the absorption edge seen in
transmission and PLE studies, and the observation that the degree of
polarization of the PL from porous Si extrapolates to the bulk Si band gap.
Most conclusively, resonantly excited PL measurements reveal phonon
replicas that demonstrate that the luminescent material in porous Si has the
electron and vibrational band structure of crystalline Si. Consequently
noncrystalline Si models and those that require strong carrier localization are
now untenable, confirming the quantum confinement model as the only viable
model for the S-band PL from porous Si. Quantitative agreement between
experimental and theoretical results requires reliable simultaneous measurement
of the optical properties of porous Si and the size and shape of the relevant
nanostructures, upon which these optical properties are sensitively dependent.
This demanding technical task has not yet been achieved. However, despite
this absence, and the additional difficulties inherent in modeling the properties
of such an inhomogeneous material as porous Si, EMT, semi-empirical and
first principles calculations have provided a strong theoretical underpinning for
the quantum confinement model. Calculations of the properties described in
the previous paragraph such as the PL energy, PL lifetime and exchange
splitting are now in qualitative agreement with experimental results. Exploitation
of the optoelectronic properties of porous Si focuses principally upon the
fabrication of EL devices. Although relatively efficient liquid-cell devices have been produced, greatest interest lies in the construction of solid-state devices. Over recent years, the efficiency of the latter has increased by more than four orders of magnitude and now approaches 0.2%. Such encouraging progress brings the possibility of all-Si optoelectronics ever closer.

3.4. Nanocrystalline silicon carbide films
3.4.1. Background

Silicon carbide (SiC) has very unique properties which bode well for applications in microelectronics and optoelectronics and have thus attracted much interest from the materials and device communities. In the microelectronic industry, silicon carbide is regarded as a promising substitute for silicon, especially in high power, high temperature, and high frequency devices [77, 78]. Recent advances in the preparation of ultra-high quality SiC single-crystals have in fact paved the way for wider uses of silicon carbide in microelectronic devices [79].

Among the different kinds of SiC nanostructures, nanocrystalline SiC which have potential applications as nanoscale light emitters were the first to receive attention and have been studied extensively in the last ten years. Optically, bulk SiC shows weak emission at room temperature on account of its indirect band gap. However, the emission intensity can be significantly enhanced when the crystallite size diminishes to several or tens of nanometers. This is thought to be caused by depressed non-radiative recombination in the confined clusters [80]. In accordance with the quantum confinement (QC) effect, photoluminescence (PL) of the crystallites with diameters below the Bohr radius of bulk excitons is shifted to blue with decreasing sizes. Consequently, wavelength-tunable emissions can be achieved by preparing crystallites with different sizes. The large band gap of SiC (2.23 eV for 3C-SiC) renders the nanocrystals a good candidate as blue and ultraviolet (UV) light emitters in displays. This is in contrast to silicon crystallites from which strong and stable emissions in these spectral ranges are difficult to achieve. Moreover, the high chemical and thermal stabilities of silicon carbide make the luminescence from these nanocrystals very stable enabling the use of the materials in harsh environments and demanding applications. Combined with their excellent biocompatibility, especially blood compatibility, low density, and high rigidity [81, 82], SiC nanocrystals are potentially useful in biology and medicine as well, for example, in bio-labelling [83, 84].

On the theoretical front, the structure and electronic properties of SiC nanostructures have been investigated employing semi-empirical and first-principle calculations. The results suggest that the band gap of SiC
Surface modification of Si-based materials by plasma gas treatments

nanostructures has a strong dependence on their sizes and surface compositions [85-87].

3.4.2. Experimental methods and microstructure

Luminescence from SiC crystallites has been experimentally studied and there are several methods to fabricate luminescent SiC crystallites. The older method is based on electrochemical etching of bulk SiC, mostly the 3C or 6H polytypes. Since the mid 1990s, several groups have attempted to attain blue emission from SiC nanocrystals produced by new techniques such as C ion implantation into bulk Si followed by etching, co-implantation of C and Si into SiO₂, C₆₀ introduction into porous silicon followed by annealing, and so on. However, the luminescent properties of SiC nanocrystals have been observed to be quite variable and strongly depend on the fabrication methods and even on the specific measurements. The emission band can span a wide spectral range from 400 to 500 nm. No luminescence exhibiting obvious quantum confinement has been reported until recently. This is in contrast to porous Si and Si nanocrystals from which quantum confinement can be more easily observed. As a binary compound, silicon carbide has complex surface states and structures. The main reasons why quantum confinement is not easily achieved in SiC are that there are many surface or defect states which dominate the luminescence and that the SiC nanocrystals are too large. Recently, colloidal 3C-SiC nanocrystals with diameters ranging from 1 to 8 nm have been fabricated via electrochemical etching of polycrystalline 3C-SiC wafers followed by ultrasonic treatment. They yield intense visible PL in a large wavelength range as predicted by the quantum confinement effect. These 3C-SiC nanocrystals that exhibit wavelength-tunable and strong luminescence have potential applications in nano-optoelectronics and biology/medicine. As an extension of this technique, SiC/polymer composite films emitting blue light have also been synthesized successfully [88].

Fourier transform infrared (FTIR) spectra of nanocrystalline SiC thin films by plasma hydrogenation are shown in Fig. 27 (from Ref. 89). An absorption peak at about 800 cm⁻¹ can be readily observed which corresponds to characteristic vibration frequency of Si-C bonds for the TO mode. The formation of Si-C bonds in the thin films is thus revealed in spite of a small shift toward a higher wavenumber. This can be attributed to a decrease in the length of the Si-C bonds as there is compressive strain possibly associated with the formation of nano-structures in the thin films. At a lower hydrogen ratio or no hydrogen addition, another salient absorption peak can be observed at about 1020 cm⁻¹, which corresponds to the characteristic vibration frequency of Si-O. As the hydrogen content increases in the plasma, the Si-O absorption peak intensity diminishes abruptly, and the Si-O absorption peak even disappears as
Figure 27. FTIR spectra of SiC films prepared with different hydrogen ratios [89].

shown in Fig. 1. It clearly indicates that plasma hydrogenation suppresses the formation of Si-O during the fabrication of SiC thin films. However, as the hydrogen ratio further increases, a weak absorption peak at the 670 cm⁻¹ which originates from amorphous SiC [90] can be observed as shown in Fig. 1(e). It is believed to be due to increased H adsorption onto the surface at a higher H₂ gas ratio thereby influencing the continuous growth and inducing the amorphous SiC phase in the thin films. Hence, suitable plasma hydrogenation conditions are necessary to suppress oxygen diffusion and formation of the amorphous phase during the growth of SiC.

The surface morphology determined by atomic force microscopy (AFM) in the contact mode from representative samples is displayed in Fig. 28. Uniform crystalline particles with nano-size are observed on the thin films prepared at the lower substrate temperature as shown in Fig. 28(a). As the substrate temperature increases, the average particles size increases and uneven surface grains are observed as shown in Fig. 28(b). The data agree with the blue shift of the FTIR peak. It further corroborates that plasma hydrogenation is an effective method to improve the composition and microstructure of SiC.

Plasma hydrogenation is believed to promote the interactions between the reactive precursors in the plasma and deposited clusters on the growing surface giving rise to faster diffusion of the deposited particles and relaxation of the growing surface. Meanwhile, the weak bond and radicals on the growing surface can be etched by plasma hydrogenation thereby reducing the disorder and improving the crystallization of SiC at lower substrate temperatures [91].
In the reaction between atomic H and the growing surface, very little energy can be released to increase the effective surface temperature. However, it can improve the mobility of the absorbed chemical radicals on the surface which is similar to the annealing effects from a chemical perspective [92]. Coper et al. have studied the role of surface-active species (surfactants) in CVD and concluded that atomic H on the growing surface exhibits the surfactant effects and decreases the surface reaction energies. The dangling bonds between the saturated β-SiC thin films and atomic H can induce negative effective surface energies which can match the surface wetting conditions [93]. Besides, a large amount of atomic H in the plasma gas can saturate the dangling bonds on the growing surface which can further suppress the formation of sp$^2$ bonds [94]. Thus, plasma hydrogenation effectively decreases the deposition temperature and improves the composition and microstructure of the cubic SiC (β-SiC) thin films, particularly the crystal particle size. It also retards the growth of amorphous carbon and oxides.

3.4.3. Photoluminescent properties

Intense room temperature PL has been observed from both SiC thin films produced on Si substrates by hot-filament CVD and porous SiC thin films formed by electrochemical anodization of SiC thin films in HF-ethanol [95]. SiH$_4$ and CH$_4$ diluted with H$_2$ are used as the precursors in the CVD process. Fig. 29 shows a series of room temperature PL spectra acquired from the anodized SiC sample during continuous irradiation by a He-Cd laser for a duration time of up to 190 min. The initial spectrum shows a strong peak at 1.9 eV, which gradually weakens with increasing irradiation time. In contrast, a new PL peak appears after UV irradiation. Its intensity is greatly enhanced,
Figure 29. A series of PL spectra acquired at room temperature under continuous UV irradiation for different periods of time from an anodized SiC thin film prepared by using a current density of 10 mA/cm$^2$ for 5 min [95].

![PL intensity vs time](image)

Figure 30. High resolution TEM image of nanocrystalline 3C-SiC embedded in an amorphous SiC matrix showing the presence of nanocrystallites in the sample [96].

10 nm

and the peak shifts from 2.5 to 2.1 eV with longer irradiation time. It should be noted that the peak energy of the new UV irradiation-induced luminescent band from the anodized SiC samples lies in the same energy range as that of the as-grown SiC thin films. Moreover, both spectra are enhanced by continuous UV irradiation. Therefore, they perhaps have the same origins, possibly induced by defect states in SiC which can be activated by UV irradiation.
Films containing nanocrystalline 3C-SiC embedded in an amorphous SiC matrix have been fabricated by hot-filament CVD employing methane and silane as the precursors [96]. The HRTEM images show that these films contain embedded nanocrystallites with an average dimension of about 7 nm (Fig. 30). X-ray photoelectron spectroscopy, X-ray diffraction, infrared absorption, and Raman scattering studies reveal that these are 3C-SiC particles. The films display strong visible emission at 2.2 eV that appears to stem from the nanocrystalline 3C-SiC. Hydrogenated nanocrystalline silicon carbide films have also been produced using a similar method. The films which contain SiC nanocrystals embedded in a-SiC:H matrix produce a strong emission peak at 2.64 eV.

Time-resolved PL spectra have been acquired from SiC nanocrystalline films deposited on Si using electron cyclotron resonance (ECR) CVD [97]. Room-temperature optical absorption measurements show a clear blueshift of the band gap with decreasing nanocluster size, as expected from the quantum confinement effect. However, the emission spectra with peak at about 2.4 eV are basically independent of the size. The temporal evolution of the dominant emission suggests double-exponential decay processes (Fig. 31). Two distinct decay times determined to be ~200 ps and ~1 ns are at least two orders of magnitude shorter than that of the bound-exciton transitions in bulk 3C-SiC at low temperature. Based on the intense emission and short decay times, it is speculated that the radiative recombination may arise from some direct transitions such as self-trapped excitons on the surface of the SiC nanocrystals.

The dramatic effects that the demonstration of tuneable efficient, room temperature light output from the material generated in 1990. Nanocrystalline SiC thin films have been deposited by plasma enhanced CVD at temperatures ranging from 80 to 575 °C using different gas flow ratios [89]. Diethylsilane is used as the source of hydrogen, and argon and helium are used as the dilution gases. The FTIR spectra indicate the formation of SiC nanocrystals embedded in the amorphous matrix at 300 °C. HRTEM confirms the existence of nanocrystallites with sizes ranging from 2 to 10 nm and TEM shows that the film consists of predominantly 3C-SiC with traces of the 4H and 6H polytypes.

Nanocrystalline 4H-SiC films have also been fabricated by plasma enhanced CVD using a mixture of SiH₄, CH₄, and H₂ precursors [98]. The Raman spectra and electron diffraction (ED) patterns indicate that the as-grown films consist of an amorphous network and single-phase crystalline 4H-SiC. The microcolumnar 4H-SiC nanocrystallites with a diameter of about 16 nm are encapsulated in the amorphous SiC network. The films display emission with a peak wavelength of 810 nm when excited by the 514.5 nm line of the Ar⁺ laser, and it is conjectured to be related to surface states or defects in the 4H-SiC nanocrystallites.
Blue-green and UV PL have been acquired from 3C-SiC layers synthesized on porous silicon by high temperature pyrolysis of polyimide Langmuir-Blodgett films in vacuum. The PL still exists after thermal treatment at 900 °C [99]. The 4H-SiC nanocrystalline films prepared by a similar method have also been reported [100]. The materials show emission bands centered at ~3.75 eV. Hydrogenated amorphous SiC thin films deposited at a low substrate temperature (100 °C) are found to exhibit red and blue-green PL [101]. Nonstoichiometric and highly disordered SiC films prepared by CVD exhibit PL composed of a series of overlapping bands from 1.8 to 3.3 eV [102].

As silicon-based microelectronic devices are approaching the physical limits, the constant push to develop better and faster devices and higher computing power has spurred the development of substituting materials. In this regard, silicon carbide is a good candidate in high-power, high-temperature, and high-frequency applications. The optical and electrical properties of nanometer-sized silicon carbide structures are particularly crucial to efficient and stable SiC nanodevices. The intense, robust and wavelength-tunable visible emission from 3C-SiC nanocrystals shows that they are good

Figure 31. Room-temperature PL decay curves of the dominant emission peaks of two samples, D and E, fabricated using flow ratios of $H_2:SiH_4:CH_4$ of 100:10:3 and 100:5:1, respectively. The solid circles represent the experimental data while the solid lines show the biexponential fitted results [97].
light sources [103] applicable to nano-optoelectronic integration. Nanocrystalline SiC films which emit visible light [104] are also promising in large area displays. Furthermore, silicon carbide is a biocompatible material [105] and biosensors made of these materials may be realized in the future. Considering the chemical stability and water-solubility, luminescent silicon carbide nanocrystals may find applications in biotechnology/medicine [88, 106].

4. Summary

As silicon-based relative devices are widely applied in microelectronic, optical and biological fields, the surface microstructure and chemical states of Si-based materials have been much attention. Recently many physical and chemical treatment methods have been exploited to investigate the surface modification of Si-based materials. Among of them, gas plasma treatment has turned out to be effective as a tool to modify the surface of Si-based materials and the relative surface properties can be obviously improved. It will accelerate the application of Si-based materials in the field of the optical, electrical and biological aspects.

Extensive studies of surface modification of Si-based materials such as single-crystalline silicon, polysilicon, amorphous silicon, porous silicon and silicon carbide and so on began in the mid 1980s and we aim at reviewing the important results published in the past 10 years in this paper. However, it should be noted that researches on the surface modification of Si-based materials by gas-plasma treatments are still in the beginning stage. Much more experimental and theoretical work is needed, especially in the aspects of biological properties. In addition, a better understanding of the various surface properties of these Si-based materials is needed in order to realize their full potentials.

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