Luminescence properties of ultrasmall amorphous Si nanoparticles with sizes smaller than 2 nm

Y. Xie\textsuperscript{a}, X.L. Wu\textsuperscript{a,b,*}, T. Qiu\textsuperscript{a,b}, Paul K. Chu\textsuperscript{b}, G.G. Siu\textsuperscript{b}

\textsuperscript{a}National Laboratory of Solid State Microstructures and Department of Physics, Nanjing University, Nanjing 210093, People’s Republic of China
\textsuperscript{b}Department of Physics and Materials Science, City University of Hong Kong, Kowloon, Hong Kong, People’s Republic of China

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Abstract

Using electrochemical etching of amorphous Si films deposited on metal molybdenum and subsequent ultrasonic treatment in water and chloroform solutions, we have fabricated the suspensions of amorphous Si nanoparticles with a size range of 1–3 nm (the probable size is at 1.7 nm with a Gaussian fitting), which are uniformly dispersed in the solvents. We examined the photoluminescence (PL) spectra of the two kinds of suspensions and found that for the chloroform suspension, the PL spectrum lasts to blueshift as the excitation wavelength decreases. For the water suspension, the PL spectrum initially shows blueshift with decreasing excitation wavelength and then remains unchanged in peak position when the excitation wavelength is below 320 nm. We attribute this difference to different surface bonding structures of amorphous Si nanoparticles, induced by the solvents. This work indicates that the surface structure has a large influence on the PL properties of Si nanoparticles with sizes smaller than 2 nm.

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1. Introduction

The goal of achieving efficient visible luminescence from Si materials has stimulated considerable efforts in understanding optical properties of Si nanostructures. Indirect gap bulk semiconductor crystalline Si (c-Si) does not show efficient light emission at room temperature. However, this situation was broken since the discovery of porous silicon with strong visible room temperature photoluminescence (PL), fabricated using simple electrochemical etching [1]. This result indicates for the first time that the luminescence properties of Si materials can be improved by quantum confinement of carriers in low-dimensional structures. Subsequently, similar visible PL was observed in porous amorphous Si nanostructures [2–5]. For Si nanocrystals, many models have been suggested to elucidate their strong luminescence origins. Some general phenomena have been concluded in mechanism. For amorphous Si nanoparticles, their luminescence mechanism is still in controversy so far. Some experimental data and theoretical investigations suggested that amorphous Si nanostructures are subjected to quantum confinement effect [6–8], while others showed that the short mean free path, order of 1 nm, of amorphous Si is responsible for no quantum confinement effect [2,4,9]. In addition, it was found that the quantum confinement mechanism alone cannot be used to explain the influence of various surface treatments and surrounding media on the luminescence properties [10–12]. Some theoretical calculations have shown that optical properties of silicon nanoparticles are highly sensitive to localized surface states, which exist in the form of self-trapped excitons and are stabilized in smaller nanoparticles due to the band gap widening [13]. Thus, it is important to disperse
amorphous Si particles into ultrasmall nanoparticles in some solvents and investigate the influence of the surface states on luminescence properties and meanwhile examine the correction of the relative theory.

In this work, we study the PL spectra of the water and chloroform suspensions of ultrasmall amorphous Si nanoparticles with a size range of 1–3 nm crumbled from fresh porous amorphous Si film. We found that for the chloroform suspension of amorphous Si nanoparticles, the PL spectrum continually blueshifts with decreasing excitation wavelength, but for the water suspension of amorphous Si nanoparticles, the continual blueshift stops when the excitation wavelength is less than 320 nm. We attribute the difference in PL property to different surface bonding structures, induced by the solvents. Our work shows that the surface structure has a large influence on the PL properties of amorphous Si nanoparticles with sizes smaller than 2 nm.

2. Samples and experiments

Porous amorphous Si samples used in this work were prepared as follows. The amorphous Si films were deposited on polished metal molybdenum substrates using RF-magnetron sputtering. The targets were B-doped, <100>-oriented c-Si wafer (1–10Ω cm). The radio frequency (RF) power was 100 W and the argon pressure 3 Pa. Electrochemical anodization of the amorphous Si films was carried out in a HF-ethanol solution (HF:H2O2:C2H5OH = 1:1:2) at a constant current density of 10 mA/cm2 for 30 min. Because HF is highly reactive with silicon oxide, H2O2 catalyzes the etching, producing smaller silicon nanoparticles (the typical average sizes in both porous c-Si and porous amorphous Si films, fabricated by using H2O instead of H2O2, are 3–5 nm [3]). At the same time, the introduction of H2O2 in the solution leads to the formation of an ideal monohydride stretching phase and the elimination of defects/impurities at the surface of porous amorphous Si [14]. As a result, completely H-passivated amorphous Si nanoparticles are formed. After dried in a stream of N2, the samples were immersed in an ultrasound water bath, in which the top porous layer, a weakly interconnected nanostructure network, was crumbled into ultrasmall particles to form a suspension of amorphous Si nanoparticles. For comparison, the nanoparticles in chloroform were also prepared using the same procedure.

High-resolution transmission electron microscopy (HRTEM) images were taken on a JEOL JEM-4000EX TEM equipment. PL spectra were measured on a FluoroMax-2 fluorescence spectrophotometer (JOBIN YVON Company) with a 150 W Xe lamp as light source. All the measurements were run at room temperature.

3. Results and discussions

Fig. 1(a) shows the HRTEM image of the amorphous Si nanoparticles taken by dropping the water suspension onto holey carbon-coated Cu TEM grid. We can see that many small dark patches appear in the image. They are uniformly dispersive and have sizes mainly in the range of 1–3 nm. The inset of Fig. 1(a) displays the selected area diffraction pattern of a typical dark patches. This pattern illustrates a highly diffusive diffraction spot, indicating that the dark patches are amorphous silicon nanoparticles. Fig. 1(b) shows a size distribution of the amorphous Si nanoparticles with a Gaussian fitting. It can be seen that the maximal probability for the nanoparticle diameter is about 1.7 nm.

To understand the optical properties of ultrasmall amorphous Si nanoparticles and the influence of the surface states on them, we examined the PL spectra of the water and chloroform suspensions of amorphous Si nanoparticles, respectively. Fig. 2 shows the PL spectra of the water suspension, taken under different excitation wavelengths. We can see that the PL peak position first
blueshifts with decreasing excitation wavelength. When the excitation wavelength is below 320 nm, the PL peak position remains unchanged. In other words, the PL peak positions, which are at about 430 nm as shown by the broken line in Fig. 2, are almost independent of the excitation energy. Fig. 3 shows the corresponding PL spectra of the chloroform suspension. It can be seen that the PL peak position monotonically blueshifts with decreasing excitation wavelength and no PL peak pinning behavior can be observed. Since the nanoparticle sizes in our current samples are almost continuously distributed (see Fig. 1(b)), this kind of monotonic blueshift of the PL peak position with excitation wavelength is understandable according to the quantum confinement effect [15]. However, the inconsistence in blueshift progress implies that different solvents have different influence on the PL properties of amorphous Si nanoparticles with sizes smaller than 2 nm. When the nanoparticle sizes decrease to 1–2 nm, the surface passivation will play an important role in determining the PL feature. After the amorphous Si nanoparticles were crumbled into water, some Si–OH bonds will form at the surfaces of amorphous Si nanoparticles, instead of original hydrogen passivation. On the contrary, ultrasound vibration in chloroform does not change the passivation status of amorphous Si nanoparticles.

To explain our experimental results, we make use of a model [16,17], combining both the quantum confinement and surface state effect, to analyze the PL peak pinning behavior in the case with higher energy excitation. We consider: (1) $\Delta E$, the amount of the band gap widening caused by the quantum confinement effect; (2) $E_b$, the exciton binding energy; and (3) $E_s$, the localization energy of the surface states. All these factors depend on the amorphous Si nanoparticle sizes, and the localized surface energy $E_s$ also further depends on the sort of surface passivation [18]. Fig. 4 shows various possible electronic transitions during PL emission from amorphous Si nanoparticles. On excitation with photons, whose energy is higher than the optical band gap of amorphous Si nanoparticle, photoexcited carriers are generated inside the particles (path a). Then, some of the photoexcited carriers directly transit from the conduction band to valence band (path b), while others relax nonradiatively to the surface states (path c) and then radiatively recombine to ground states giving PL (path d). Since surface to volume ratio increases with decreasing the nanoparticle size, the contribution of path d to PL is highly enhanced when the size is ultrasmall. So, we neglect the contributions due to direct transitions (path b).

Based on the above assumptions, the emitted photon energy from one amorphous Si nanoparticle will be lower than the band gap energy by an amount of the exciton binding energy $E_b$ and the localization energy $E_s$ of the surface states. The emitted photon energy from one

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**Fig. 2.** PL spectra of the water suspension of amorphous Si nanoparticles. The excitation wavelengths have been marked in the figure.

**Fig. 3.** PL spectra of the chloroform suspension of amorphous Si nanoparticles. The excitation wavelengths have been marked in the figure.
amorphous Si nanoparticle can then be given as
\[ E_{pl} = E_g + \Delta E - E_b - E_s, \]
where \( E_g \) is bulk amorphous silicon band gap. According to the quantum confinement effect and effective mass theory [19], \( \Delta E = C/d^2 \), where \( d \) is the particle size and \( C \) is the confinement parameter. Following the experiment result of Park et al. [6] regarding the quantum confinement on amorphous silicon nanoparticles (this result has been confirmed by the theoretical calculation of Nishio and Koga [8], we take \( C = 2.40 \) eV and \( E_g = 1.56 \) eV. Exciton binding energy \( E_b \) increases monotonically as the particle size decreases. The increase is more pronounced for smaller-size nanoparticles. According to the theoretical calculations for crystalline silicon [20], \( E_b \) becomes inversely proportional to the square of crystallite size when the size < 4 nm. The presence of surrounding media for amorphous Si particles further complicates the analysis of the observed PL data. For c-Si nanoparticles, oxygen termination may have several effects including the formation of the surface states and a modification of the electronic structure of the c-Si interior states [21–24]. Moreover, when the sizes of nanoparticles are smaller than the bulk exciton Bohr radius, oxygen atoms at the interface induce the localization of excitons near the interface [13]. For bulk amorphous Si, the exciton model was proposed by Street [25]. The electronic interaction at the interface (Si–OH bonds) induces strong exciton localization [26] and thus affects the luminescence property of amorphous Si nanoparticles. Therefore, the localization degree of surface states, manifested by \( E_s \), strongly depends on the type of surface passivation. And, the localization energy \( E_s \) of amorphous Si nanoparticles whose surfaces are terminated with hydrogen is much lower than that of amorphous Si nanoparticles whose surfaces are terminated with oxygen [18]. Based on above analysis, we can roughly estimate the PL peak-position dependence on amorphous Si particle sizes. For such nanoparticles whose surfaces are terminated with oxygen, when the sizes reduce to 1.2 nm, the increment of \( (E_b + E_s) \) compensates that of \( \Delta E \). As a result, the emitted photon energy always stays at 2.9 eV (430 nm) when the particle size further decreases. For the nanoparticles with hydrogen termination, since \( E_s \) is very low compared with \( \Delta E \) even for the ultrasmall size [18], the emitted photon energy always increases with decreasing the nanoparticle sizes.

4. Conclusions

We have investigated the light-emitting properties of the ultrasmall amorphous Si nanoparticles with sizes of 1–3 nm which are dispersed in water and chloroform solutions. The luminescence properties of the amorphous Si nanoparticles are highly dependent on their sizes and the surface passivation status. The continuously tunable emission in a range from 400 to 460 nm and the stability of luminescence are new features of this kind of nanomaterials. The obtained results can be expected to have applications in nanodevices and biomaterials.

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