AlN thin films fabricated by ultra-high vacuum electron-beam evaporation with ammonia for silicon-on-insulator application

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Abstract

The application of silicon-on-insulator (SOI) substrates to high-power integrated circuits is hampered by the self-heating effect due to the poor thermal conductivity of the buried SiO2 layer. We introduce aluminum nitride (AlN) thin films formed by ultra-high vacuum electron-beam evaporation with ammonia as an alternative. The chemical composition, surface morphology, and electrical properties of these films were investigated. The film synthesized at 800 °C shows a high AlN content, low surface roughness with a root-mean-square value of 0.46 nm, and high electrical resistivity. Based on thermodynamic analysis and our experimental results, the mechanism of AlN formation is proposed.

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1. Introduction

Silicon-on-insulator (SOI) technology possesses many advantages over bulk silicon technology such as the reduction of parasitic capacitance, excellent sub-threshold slope, elimination of latch up, and resistance to radiation [1]. Hence, it is expected to become a popular substrate materials for microelectronic devices in the near future. However, the use of the SOI in high-power integrated circuits is hampered by the self-heating effect caused by the poor thermal conductivity of the insulating SiO2 layer that is approximately 100 times less than that of silicon [2]. Moreover, as the device geometries shrink and transconductance as well as current density increase with MOS scaling, the self-heating effect becomes more pronounced. Hence, in order to develop integrated circuits with on-chip power devices, it is important to investigate an alternative buried insulator with better thermal conductivity [3].

Recently, ion-cut has become one of the major SOI fabrication techniques [4]. This process furthermore opens the window for the synthesis of many other exciting materials such as silicon-on-glass [5],
germanium, silicon carbide, diamond thin films [6], and even three-dimensional devices [7]. The ion-cut technique has been reported in detail elsewhere [4,8]. Using this process, another insulator with higher thermal conductivity can substitute for the buried silicon dioxide. One of the interesting buried insulators is aluminum nitride (AlN) with a thermal conductivity about 100 times higher than that of SiO₂ (136 W/m K versus 1.4 W/m K) and roughly equal to that of silicon itself (145 W/m K). In addition, AlN has excellent thermal stability, high electrical resistance and a coefficient of thermal expansion close to that of silicon. Thus, the use of AlN as the buried insulator in SOI may mitigate the self-heating penalty of the SOI materials enabling more general and high-power applications.

Various techniques have been reported for the synthesis of AlN films, including chemical vapor deposition (CVD) [9,10], reactive magnetron sputtering [11], plasma assisted molecular-beam epitaxy (PAMBE) [12], etc. However, most of the previous work used sapphire or SiC as the substrate. Electron-beam evaporation is an efficient way of deposition thin films on various types of substrates. Recently, the deposition of high-quality AlN on Si by gas-source molecular-beam epitaxy with ammonia has been reported [13]. In the work reported in this paper, a similar but simpler technique employing ultra-high vacuum electron-beam evaporation was utilized to synthesize AlN thin films on Si substrate. The chemical composition was investigated at different deposition temperatures and two of the critical parameters in the ion-cut process, surface morphology and electrical resistivity, were studied. The nitridation reactions of Al were also discussed in this paper based on thermodynamic calculations and the experimental results.

2. Experimental

P-type Si (1 0 0) wafers, with resistivity of 2–10 Ω cm, were used as substrates. They were degreased and chemically cleaned using a standard RCA process employing a conventional HF-last step to leave a smooth H terminated surface. Prior to deposition, the main vacuum chamber UMP500P (made by Balzers) was evacuated to below 10⁻⁹ Torr. The substrate was subsequently loaded into the evaporation chamber through a load-lock mechanism. High purity (>99.99%) solid sintered Al pellets were used as the evaporation source and ultra-pure ammonia (99.9995%) was used as the reactive gas. Before ammonia was bled in, one to two monolayers of Al were deposited on the substrate surface to prevent the formation of Si₃N₄. Then, ammonia gas was introduced through a leak valve to maintain the working pressure at 8 × 10⁻⁵ Torr. Al was subsequently evaporated by an electron gun and reacted with ammonia to form AlN on the substrate. The deposition rate of AlN monitored by the quartz crystal monitor was set to 0.05 nm/s, and the deposition time was about 60 min. Two deposition temperatures, 800 °C (sample 1) and room temperature (RT, sample 2), were compared.

The chemical composition of the AlN thin films was investigated by X-ray photoelectron spectroscopy (XPS). The microstructure and surface morphology were evaluated by X-ray diffraction (XRD) and atomic force microscopy (AFM). Spreading resistance profiling (SRP) was employed to determine the electrical properties and the film thickness. The current–voltage (I–V) characteristics were measured by producing an Al/AlN/Si MIS structure.

3. Results and discussion

The XPS analysis is carried out on Microlab MK II spectrometer using Mg Kα radiation source with energy of 300 W and calibrated by C 1s line at 284.6 eV. The vacuum chamber pressure was always better than 4 × 10⁻¹⁰ Torr during the whole acquisition time. To acquire the depth profiles, the AlN samples were sputtered by a 4 kV argon ion beam. Fig. 1 shows a survey spectrum of the two samples deposited at RT and 800 °C. In addition to the salient Al 2p and N 1s lines, O Auger and photoelectron peaks can also be observed. O contamination is unavoidable in the preparation of AlN film due to the extremely high reactivity of Al with oxygen. Oxygen may originate from adsorbed gas molecules on the substrate and the inner wall of the vacuum chamber, impurities (O₂ and H₂O) in ammonia, as well as the residual vacuum. We notice that when the substrate temperature is RT, the N 1s intensity is much weaker than that
of O 1s, which indicates that a major component in the film is Al$_2$O$_3$. This result will be confirmed further by high-resolution core-level spectra of Al 2p and N 1s. Fig. 2 shows the Al 2p photoelectron spectra acquired from sample 1 (solid line) and sample 2 (dash line). The solid line has been fitted using two components based on a Gaussian curve-fitting program. The low binding energy peak (73.8 eV) arises from aluminum atoms bonded to nitrogen atoms as shown in previous studies [14,15]. The higher binding energy peak (75.1 eV) is related to aluminum atoms bonded to oxygen atoms. No Al–Al bonds that would appear at 72.9 eV can be found. As for sample 2, only one peak appears at 75.1 eV, which corresponds to the binding energy of the Al 2p state in the Al–O bond. The N 1s photoelectron spectra are displayed in Fig. 3. Similarly, two components have been resolved for sample 1. The N 1s peak observed at 396.5 eV corresponds to the binding energy of N 1s in N–Al, and the other peak at 398.3 eV is N 1s indicates N–N [16]. It should be noted here that the N 1s intensity of sample 2 is much less than that of sample 1 under the same measurement conditions. Hence, it can be inferred that sample 2 is composed of mostly Al$_2$O$_3$, not AlN.

The corresponding depth profiles of Al, N and O in these two samples are depicted in Fig. 4. The composition with depth in sample 1 is nearly uniform. Beneath the surface, the amount of O is observed to be below 10%, which is in agreement with our former XPS results. The higher structural disorder confirmed by XRD analysis (not shown here) in the AlN film grown at 800 °C can be attributed to the presence of O contamination. In sample 2, the measured O to Al ratio is about 1.5, which again confirms that the major component is Al$_2$O$_3$. A series of Al 2p spectra taken at different depths (40 nm intervals) from sample 1 are shown in Fig. 5. From the film surface to the interface, the Al 2p peaks shift from 74 to 74.3 eV initially, and then decrease to 74.2 eV. The variation of the binding energy can be correlated to components such as aluminum oxynitride. All in all, the XPS results confirm the successful synthesis of AlN at 800 °C with no detectable metallic aluminum in the films. However, when the substrate is at RT during deposition, the resulting film is dominantly Al$_2$O$_3$.

The 10% oxygen concentration revealed by XPS is unexpected in view of the deposition conditions mentioned above. It may be attributed to the high affinity of Al to oxygen resulting in the formation of surface oxide when the AlN films are exposed to air. Another likely reason is that even though the chamber vacuum is quite good, the free energy of Al–O is much more negative than that of Al–N, and so Al$_2$O$_3$ will be formed despite a relatively low oxygen amount in the residual vacuum.
The long-term goal of our work is to fabricate microelectronics-quality Si/AlN/Si wafers using the ion-cut process. In order to be successful in direct bonding of AlN and Si, the deposited AlN thin films must exhibit low surface roughness [17]. Therefore, AFM was performed to examine the surface topography of our AlN films. Fig. 6 depicts the AFM image of the film synthesized at 800 °C. It can be observed that the surface of the AlN film is smooth and uniform with a surface roughness RMS value of 0.46 nm.

In addition to surface morphology, high electrical resistivity is the important and necessary property of
the AlN thin films. Therefore, SRP (shown in Fig. 7) was employed to study the electrical properties and thickness of the film. For the AlN film formed at 800 °C, a highly resistive structure with a spreading resistance as high as $6 \times 10^5 \Omega$ is found from the surface to a depth of around 200 nm, suggesting excellent dielectric properties and the formation of AlN. After 200 nm, the spreading resistance drops abruptly to about $7 \times 10^4 \Omega$ that corresponds to the Si substrate, indicating a very sharp AlN/Si interface and that the thickness of this film is about 200 nm. The electrical breakdown field reflects the insulated property of thin film and it can be determined by the current–voltage ($I$–$V$) characteristics measured from our Al/AlN/Si MIS structure. Fig. 8 displays the $I$–$V$ characteristics of the AlN films deposited at 800 °C. It can be observed that the breakdown voltage is 86 V. The breakdown field $E_B$ can be calculated from $E_B = V_B/d$, where $d$ is the thickness of AlN thin film and $V_B$ is the breakdown voltage. The breakdown field of our sample is about 4.3 MV/cm, which compares reasonably well with previously reported results [18,19]. Hence, the AlN thin film fabricated by our method has a high electrical resistivity and is a suitable substitute for SiO₂ in SOI.

In our experiments, ammonia gas was employed instead of the more common nitrogen used in some other studies [20–22]. The use of ammonia serves to lower the reaction temperature and achieve a higher conversion of Al. This is because of the lower N–H bonding energy in NH₃ compared to the N–N bonding energy in N₂, and so less energy is required to break the bonds. Our results show that the RT film is predominantly Al₂O₃. This is believed to be due to the insufficient energy to dissociate the N–H bonds. Hence, Al only reacts with oxygen in the residual vacuum to form Al₂O₃. According to the experimental conditions and results, the nitridation reaction of Al and mechanism of AlN formation are proposed here.

In electron-beam evaporation, a current is sent through a tungsten filament in the vacuum chamber to produce thermionic emission of electrons. The
electrons are focused and directed towards the crucible containing the Al pellets by means of permanent magnets or electromagnets. The source is heated and some fractions of the Al atoms gain enough kinetic energy to leave the crucible. These Al atoms react with ammonia gas in the chamber to form AlN. We can assume that there are mainly two situations of the dissociation of NH$_3$, one preceding the nitridation
reaction of Al and the other is simultaneous with nitridation reaction. These two reactions can be written as Eqs. (1) and (2), respectively [23]:

\[
\text{Al} (s) + \frac{1}{2} \text{N}_2 (g) + \frac{3}{2} \text{H}_2 (g) \rightarrow \text{AlN} (s) + \frac{3}{2} \text{H}_2 (g)
\]

(1)

\[
\text{Al} (s) + \text{NH}_3 (g) \rightarrow \text{AlN} (s) + \frac{3}{2} \text{H}_2 (g)
\]

(2)

When the system pressure is not 1 atm, the Gibbs free energy change can be written as:

\[
\Delta G = \Delta G^\circ + RT \ln P
\]

(3)

\[
\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ
\]

(4)

where \(\Delta H^\circ\) and \(\Delta S^\circ\) are the standard enthalpy change and entropy change, respectively, \(R\) the gas constant which depends on the pressure \((P)\), temperature \((T)\) and volume. According to thermodynamic calculations, the Gibbs free energy changes for reactions (1) and (2) at 800 °C and 8 × 10⁻⁶ Torr are −334.5 and −395 kJ/mol, respectively. The data of thermodynamic properties used here are extracted from JANAF Thermochemical Tables [24]. It can be seen that the free energy change associated with reaction (2) is much more negative than that of reaction (1), thereby providing a driving force for the dissociation of NH\(_3\) when it comes in contact with Al. This thus enhances its thermal dissociation into reactive nitrogen radicals such as NH\(_2\), NH, and N. Moreover, because the dissociation of NH\(_3\) is stepwise, the dissociation energies of the N–H bonds in NH\(_3\), NH\(_2\), and NH are 402, 375 and 356 kJ/mol, respectively. It is obvious that only reaction (2) can provide enough energy for the dissociation of NH\(_3\). That is to say, the dissociation of NH\(_3\) occurs in concert with nitridation. In addition to the above thermodynamic calculations, another experiment was done to confirm our observation. We repeated our experiments using the same conditions but replacing NH\(_3\) with N\(_2\). Subsequent XPS analysis did not reveal the formation of AlN and so ammonia could not decompose prior to the nitridation reaction.

From our thermodynamic analysis and experimental results, the mechanism of AlN formation is proposed. Initially, Al vapor is formed when the electron beam impacts the Al charge. The dissociation of NH\(_3\) occurs near the Al particles on the substrate at 800 °C, and the reactive N (NH\(_2\), NH) radicals as well as H radicals are formed [reaction (5) shown below]. Then Al reacts with N radicals to form AlN [reaction (6)] on the Si surface and deposition ensues. Meanwhile, H radicals react with NH\(_3\) molecules to promote the dissociation of NH\(_3\) and new N radicals form [reaction (7)]:

\[
\text{NH}_3 (g) \rightarrow \text{N} (g) + 3 \text{H} (g)
\]

(5)
Al (s) + N (g) → AlN (s)  
\( \text{(6)} \)

\[ \text{NH}_3 (g) + 3\text{H} (g) \rightarrow \text{N} (g) + 3\text{H}_2 (g) \]  
\( \text{(7)} \)

Note that the sum of reactions (5)–(7) is reaction (2). The higher substrate temperature during deposition thus favors the formation of AlN more favored to form.

4. Conclusion

We have studied the formation of AlN thin film on silicon using nitridation of Al by ultra-high vacuum electron-beam evaporation with ammonia. The substrate temperature plays an important role. The sample deposited at room temperature comprises predominantly aluminum oxide whereas that deposited at 800 °C contains AlN. The 800 °C films display outstanding surface topography with RMS roughness value below 0.5 nm as well as high electrical resistivity. Both of these properties are vital to the success of AlN to replace SiO\(_2\) in SOI. Based on our results and thermodynamic analysis, the mechanism of AlN formation is proposed.

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References