Synthesis of aluminum nitride films by plasma immersion ion implantation–deposition using hybrid gas–metal cathodic arc gun

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Aluminum nitride (AlN) is of interest in the industry because of its excellent electronic, optical, acoustic, thermal, and mechanical properties. In this work, aluminum nitride films are deposited on silicon wafers (100) by metal plasma immersion ion implantation and deposition (PIIID) using a modified hybrid gas–metal cathodic arc plasma source and with no intentional heating to the substrate. The mixed metal and gaseous plasma is generated by feeding the gas into the arc discharge region. The deposition rate is found to mainly depend on the Al ion flux from the cathodic arc source and is only slightly affected by the N₂ flow rate. The AlN films fabricated by this method exhibit a cubic crystalline microstructure with stable and low internal stress. The surface of the AlN films is smooth with the surface roughness on the order of 1/2 nm as determined by atomic force microscopy, homogeneous, and continuous, and the dense granular microstructures give rise to good adhesion with the substrate. The N to Al ratio increases with the bias voltage applied to the substrate. A fairly large amount of O originating from the residual vacuum is found in the samples with low N:Al ratios, but a high bias reduces the oxygen concentration. The compositions, microstructures and crystal states of the deposited films are quite stable and remain unchanged after annealing at 800 °C for 1 h. Our hybrid gas–metal source cathodic arc source delivers better AlN thin films than conventional PIIID employing dual plasmas. © 2004 American Institute of Physics.

I. INTRODUCTION

AlN is attractive in the industry because of its electrical properties, high thermal conductivity (0.67–2 W/cm K), wide band gap (6.2 eV), good acoustic velocity, high hardness, and high wear resistance. AlN thin films are thus widely found in many commercial products such as surface acoustic wave devices, buried dielectric layers in future silicon-on-insulator, thin buffer layers for GaN epitaxial growth, hard films, optical films, etc. Synthesis of AlN films can be carried out using a number of techniques including plasma-enhanced chemical vapor deposition, metalorganic chemical vapor deposition, pulsed laser deposition (PLD), ion-beam assisted deposition, molecular beam epitaxy (MBE), and magnetron sputter deposition.

Metal plasma immersion ion implantation–deposition (Me-PIIID), a hybrid process combining cathodic arc deposition and plasma immersion ion implantation, is a surface modification technology. It has been used to fabricate various types of metal, alloy and compound films. This article reports the deposition of aluminum nitride using Me-PIIID utilizing a hybrid gas–metal cathode arc gun and without intentional substrate heating. The metal and gas species are generated simultaneously from the cathodic arc gun by feeding nitrogen gas into the arc discharge region. The characteristics of the films prepared by this method and the effects of the N₂ gas flow rate on the AlN film deposition dynamics are investigated.

II. EXPERIMENTAL APPARATUS

The experiments were conducted using the PIII-D equipment at the City University of Hong Kong. The apparatus consists of a hybrid metal–gas cathodic arc gun, rf source, a cylindrical processing chamber with a diameter of 1 m and height of 1.2 m, a turbo-molecular pump vacuum system, power supplies, and control systems. The hybrid cathodic arc plasma gun comprises an Al cathode 10 mm in diameter, a stainless-steel anode about 56 mm in diameter in front of the cathode, and an additional gas inlet at the cathode flange. A curved magnetic filter is inserted between the cathodic arc gun and the main vacuum chamber to minimize the transmission of macroparticles from the source to the sample. These macroparticles are a byproduct of the arcing process on the cathode and are neutral. They are not affected by the magnetic field and thus strike the wall of the curved duct instead of being transmitted through the curved filter. Hence, the deposited films would be free of Al macroparticles. The schematic of the hardware is depicted in Fig. 1. The metal plasma is produced by means of cathodic arc discharge touched off by a high...
voltage trigger electrode. Aluminum is vaporized and almost fully ionized due to the high temperature of the cathode arc. At the same time, the metal arc plasma efficiently ionizes the nitrogen molecules bled from the backside of the gun to produce nitrogen ions. The Al, N, as well as other atomic and molecular ions with single and multiple charge states diffuse through the magnetic filter with a kinetic energy of approximately 25–50 eV per charge state and subsequently impinge into the substrate with the added sample bias to form the AlN films. In the experiments, the discharge current of the metal cathodic arc gun was 100 A, the magnetic field strength in the duct was 100 G, and the bias voltage at the duct was 20 V. The cathodic arc gun was operated in a pulsed mode with a duration of 300 ms and repetition frequency of 60 Hz. The sample holder was biased at different negative dc high voltages that determine the incident energies of the of Al and N ions.

The existence of alumina in our AlN films is unavoidable due to the extremely high reactivity of Al with oxygen and nonultrahigh vacuum conditions in our vacuum chamber. Oxygen comes from adsorbed gas molecules on the substrate and the inner wall of the vacuum chamber, gas leaks, as well as the residual vacuum. In our work, the following measures were taken to minimize residual oxygen and carbon contamination:

1. The liners on the inner wall of the vacuum chamber were mechanically cleaned. Before deposition, a rf-assisted hydrogen glow discharge was utilized to clean the interior of the vacuum chamber.

2. The substrates, single crystal (100) silicon, were cleaned with anhydrous acetone, HF, de-ionized water, and anhydrous alcohol before loading into the vacuum chamber (Fig. 1).

3. High purity N₂ (99.999% purity) gas was used to flush the vacuum chamber walls several times prior to deposition.

4. The predisposition base vacuum was less than 1.5 × 10⁻⁵ Torr, and high purity argon was bled into the vacuum chamber at a flow rate of 20 sccm. The rf glow was then ignited in the plasma chamber while the sample was biased to −1 kV dc for 1/2 h to perform surface sputter cleaning.

5. In the initial stage of the deposition, the sample was biased to −1.5 kV for 10 min to perform ion mixing. In this process, the energy loss by both the implanted Al and nitrogen ions create an ion-mixed zone with graded composition in lieu of an abrupt AlN/Si interface. This process enhances the adhesion of the film deposited in the latter step that ensued using −0.5 kV dc.

6. After deposition, high purity nitrogen was bled into the chamber to minimize exposure to water or oxygen before the samples were unloaded to conduct various types of tests. In spite of the precautions, the incorporation of oxygen cannot be eliminated and will be discussed in the next sections.

To evaluate the quality, structure, and composition of the AlN films, they were characterized using Fourier transform infrared spectroscopy (FTIR), x-ray diffraction (XRD), atomic force microscopy (AFM), and x-ray photoelectron spectroscopy (XPS).

III. RESULTS

FTIR is employed to investigate the characteristic vibrational frequencies of the bonded atoms and lattice vibrations in ionic crystals. The spectra were recorded in the transmission mode using a Perkin Elmer 1600 series FTIR spectrometer from the films of thickness of about 90 nm deposited below 200 °C (depending on deposition conditions). Background subtraction was performed by acquiring a spectrum from a Si substrate of the same orientation and thickness. Figure 2 displays the infrared transmission spectrum of the aluminum nitride film deposited by Me-PIIID at different nitrogen flow rates. The transparency at near infrared (IR) is more than 95% and quite high. A strong and sharp transmis-
sion peak at 668 cm\(^{-1}\) emerges and it is very close to the characteristic value of aluminum nitride of 667 cm\(^{-1}\).\(^{24}\) There are no other obvious peaks even by extending the scanned wavelength range. The intensity and position of the Al–N peak is about the same in the samples deposited at different flow rates with a full-width at half maximum (FWHM) of about 2.6 cm\(^{-1}\). As reported in the literature,\(^ {25-27}\) a small value of FWHM is indicative of good crystal quality. In addition, some studies have revealed that the internal stress of the films is related to the peak shift as crystal imperfection may result in variations in the vibration bands.\(^ {25,28,29}\) Our results thus show that in the hybrid gas–metal cathodic arc source, the nitrogen flow rate does not significantly affect the AlN film growth. Moreover, the narrow and fixed peaks in the IR spectra indicate that this technique can be used to prepare stable films with low stress.

XRD was performed to evaluate the phase and structure of the films on a Siemens 500/501 diffractometer with a Cu\(\text{K}\alpha\) x-ray with a fixed incident angle of 1°. Though not shown here, two diffraction peaks at 2\(\theta\) = 38.6°, 43.9°, and two very weak peaks at 2\(\theta\) = 66.2°, 78.4°, can be observed in the XRD spectra of all the samples due to the thin film (~90 nm). The diffraction peak positions correspond to orientations of (111), (200), (220), and (311) of the cubic AlN crystal,\(^7\) and so the AlN films prepared by Me-PIIID with the hybrid source at lower than 200 °C are c-AlN crystalline films. After postannealing at 500 and 800 °C for 1 h under a nitrogen ambient (1463 Pa), no changes in the XRD spectra can be observed, thereby indicating that the structure is quite stable.

AFM was used to characterize the topography and roughness of the film surface. An AFM (SPA400) was operated in the contact mode at room temperature under dry nitrogen. The AFM image of the deposited AlN film in Fig. 3 shows smooth, homogeneous, continuous, and dense granular microstructures as well as good adhesion with the substrate. The root mean square (rms) surface roughness over an area of 2\(\times\)2 \(\mu\text{m}^2\) is 0.56 nm and much lower than that accomplished by other deposition methods.\(^7,10,30\) After annealing at 500 and 800 °C for 1 h, the AFM images and the rms surface roughness do not change significantly, and once again demonstrate the thermal stability of the surface as well as structure of the deposited films.

The samples were analyzed by XPS to determine the elemental composition in depth as well as the chemical states of the elements. The analyses were performed on a PHI 5802 x-ray photoelectron spectrometer with a monochromatic Al\(\text{K}\alpha\) source. The XPS survey spectrum in Fig. 4 shows that Al, N, and O are the main elements in the films. There is a fairly low carbon content (less than 5%) that perhaps originates from adsorption upon exposure to air after deposition. The thickness of the AlN films determined from the XPS depth profiles is about 90 nm using a nominal sputtering rate of 6 nm/min based on previous similar analyses. The deposition rate is thus calculated to be 0.47–0.55 nm/min, which mainly depends on the Al\(^{+}\) ion flux density and decreases with increasing N\(_2\) flow rate. When the nitrogen flow rates changes from 10 to 40 sccm, the N to Al concentration ratios vary from 0.40 to 0.52. The N 1\(s\) photoelectron signal is displayed in Fig. 5. The N 1\(s\) peak observed at 397.3 eV corresponds to the binding energy of N 1\(s\) in the N–Al bond,\(^ {31}\) and the other peak at 399.5 eV is N 1\(s\) in the N–N bond.\(^ {31}\) The results corroborate the formation of AlN. The

![FIG. 3. Surface topography revealed by atomic force microscopy (AFM) on a 1\(\times\)1 \(\mu\text{m}^2\) scanned area of the AlN film deposited using a nitrogen flow rate of 30 sccm.](image-url3)

![FIG. 4. XPS survey spectrum acquired from the AlN film deposited using a flow rate of 40 sccm after sputter cleaning for 2 min.](image-url4)

![FIG. 5. XPS spectrum of N 1\(s\) at a sputtered depth of 40 nm of the AlN film deposited using a nitrogen flow rate of 40 sccm.](image-url5)
Al$_2$p signal in Fig. 6 shows two peaks. The peak at 74.1 eV is related to aluminum atoms bonded to nitrogen atoms. The value is consistent with reported values at 73.9$^{32}$ and 74.4 eV.$^{33,34}$ The higher binding energy (75 eV) peak is related to Al–O.$^{31}$ No metallic aluminum which would be found at 72.9 eV for the Al$_2$p peak can be found. Figure 7 shows the N 1$s$ and Al$_2$p peaks after some sputtering. The N 1$s$ peak at 397.3 eV does not change with depth but the Al$_2$p peak shifts from 74.6 to 74.9 eV, indicating a change in the Al$_2$p bonded to O. All in all, the XPS results confirm the successful synthesis of AlN with no detectable metallic aluminum in the films. If the experiments were conducted using a conventional cathodic arc plasma source and separate nitrogen plasma sustained in the vacuum chamber as commonly practiced in traditional PIIID, the existence of metallic aluminum in the film would be inevitable. It should, however, be noted that several tens of atomic percent of oxygen (it can be roughly estimated from the integrated peak area of the survey spectrum) is found in our AlN films in spite of a base pressure of 1.5 $\times$ 10$^{-5}$ Pa and the use of high purity nitrogen of 99.999%. Our films may thus be categorized as aluminum oxynitride technically speaking. The amount of unintentional oxygen can be reduced by designing PIII chamber with better vacuum. Further studies such as Rutherford backscattering spectrometry and transmission electron microscopy can be used to determine more clearly the microstructure, phases and crystal quality of the films and the work will be conducted in our laboratory.

**IV. DISCUSSION**

In conventional plasma immersion ion implantation–deposition, metal compound films such as titanium oxide and aluminum nitride are typically deposited using the metal ions produced from a cathodic arc plasma source and gas ions from another plasma sustained separately in the vacuum chamber. This, however, may not be the best approach, and in this article, we report a different way by mixing the gas ions with the metal ions in the arc plasma. As discussed in Sec. III, aluminum nitride thin films fabricated using this technique are superior to those produced by other methods, including conventional PIIID. The dynamics of the deposition process, particularly that associated with the deposition temperature, is discussed in this section.

Plasma deposition is a nonequilibrium process and a low substrate temperature does not provide adequate energy thermodynamically for the growth of crystalline AlN. Therefore, a high substrate temperature normally above 800°C is usually employed in most deposition methods including PLD, rms, and MBE. However, such a high temperature may not be desirable and in fact precludes a wider acceptance of AlN in the semiconductor industry.$^7$ Using our modified hybrid gas–metal cathodic arc plasma source, aluminum nitride films with cubic crystalline microstructure can be deposited on silicon (100) substrate by Me-PIIID at a substrate temperature of less than 200°C. The energy required for the formation is believed to come from the energetic Al$^+$, N$_2^+$/N$^+$, as well as the various Al atomic and AlN molecular ions with single and multiple charge states produced by the cathodic arc source. The cathodic arc is a very efficient source and produces a high percent of ions. The kinetic energy of ions emitted from a cathodic arc is typically about 25–50 eV per unit charge and when ions impinge into the substrate with the added bias applied to the sample, the mo-
bility is greatly enhanced leading to the formation of polycrystalline AlN, which is normally not observed at room temperature. Here, the ion kinetic energy can be monitored using a time-of-flight technique and the ion penetration depth in the substrate is more dependent on the magnitude of the applied bias. The magnetic filter eliminates macroparticles from reaching the substrate, making the film smooth, homogeneous, and crack free. The grain size is quite fine and the dense granular microstructure permits good adhesion with the substrate. In other experiments employing activated reactive ion plating with a cathodic arc source without a magnetic filter at substrate temperature of 700–800 °C, a large number of cauliflower-like features with average sizes of approximately 10–20 μm were observed on the film surface. In contrast, the surface roughness of the films produced by our modified Me-PIIIIID process is 0.56 nm. The magnetic filter and lower deposition rate due to the low duty ratio gives rise to a uniform film with extremely low internal stress that can be inferred from the very narrow absorption peak and peak shift from 667 to 668 cm⁻¹ in the FTIR spectra. The minute peak shift does indicate the existence of small compressive stress in the film.

Our films are found to contain about several tens of percent of oxygen that can be attributed to outgassing from exposed surfaces, leakages in the system, as well as oxygen containing species in the residual vacuum, although extra steps have been taken to reduce the oxygen level, for example, by pumping the chamber to 1.5 × 10⁻⁵ Torr before deposition, cleaning, and flushing, as well as using 99.999% pure N₂ gas in the experiments. When the nitridation or oxidation process of metals reaches a balance, the variation of the reaction free energy ΔG¹ for nitridation and oxidation depends on the N₂ partial pressure P(N₂) and oxygen partial pressure P(O₂), respectively.

\[ ΔG¹(N₂) = RT \ln P(N₂), \]
\[ ΔG¹(O₂) = RT \ln P(O₂). \]

For a temperature of 200 °C,

\[ ΔG¹(N₂) = -241 \text{ kJ/mol}, \]
\[ ΔG¹(O₂) = -1018 \text{ kJ/mol}. \]

We can obtain the partial pressure at which the nitridation or oxidation reaction stops: P(N₂) = 2.43 × 10⁻²⁷ Pa and P(O₂) = 3.75 × 10⁻¹¹³ Pa. A large amount of oxygen in the film suppresses the incorporation of nitrogen to the Al ratio, especially under a low bias voltage like 500 V. In our experiments, the N:Al ratio is 0.5 at 500 V, but increases to 1.14 at 5 kV.

In recapitulation, using a hybrid gas–metal cathodic arc source in which nitrogen gas is bled from the back to mix with the aluminum ions, aluminum nitride films with cubic crystalline microstructure are deposited on crystalline silicon (100) substrate without intentional substrate heating. The surface roughness as determined by AFM is 0.56 nm. The surface of the deposited AlN films is very smooth, homogeneous, and continuous, and the dense granular microstructure bodes well for good adhesion with the substrate. The compressive stress in the films is observed to be extremely low and uniform. The deposition rate of AlN films mainly depends on the Al ion flux from the cathodic arc source, and is only slightly affected by the N₂ flow rate. The N to Al ratio in the films increases with the bias voltage applied to the substrate. A high level of O is found in films with a low N:Al ratio, but diminishes at a higher bias voltage. The compositions, microstructures, and crystal states are thermally stable even after annealing at 800 °C for 1 h. Our results show that the modified cathodic arc source produces AlN films with excellent quality and stability.

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