I. INTRODUCTION

Processing of high-quality metal nitride thin films on silicon is under intense investigation currently, because of desirable optoelectronic, thermal, and acoustical properties. Aluminum nitride (AIN, having hexagonal wurtzite structure, lattice constants are \(a = 3.112 \text{ Å} \) and \(c = 4.982 \text{ Å}\)), with a band gap of \(6.2 \text{ eV}\) and high surface acoustic wave (SAW) velocity (\(6 \times 10^5 \text{ cm/s}\)) offers tremendous potential for UV light emitting and SAW devices. Additionally, AIN has high thermal conductivity (320 W/mK), high thermal stability (up to 2200 °C), high resistivity (10^13 Ω cm), high dielectric strength (14 kV/mm), and high chemical inertness. Its hardness and thermal coefficient of expansion (2.56 \times 10^{-6}/K) are comparable to that of silicon. The above properties make AIN an ideal candidate for applications in microelectronics ranging from optoelectronic and high temperature devices to electronics packaging. High quality epitaxial heterostructures are required to fully realize these microelectronic applications of AIN. Various techniques have been reported for the synthesis of AIN films. These include chemical vapor deposition (CVD), plasma assisted CVD, metalorganic CVD, reactive dc-magnetron sputtering, plasma assisted molecular beam epitaxy (MBE), laser chemical vapor deposition, and pulsed laser deposition (PLD). The PLD lends itself to low-temperature processing because average energy of particles in the laser evaporated species is considerably higher (~10 eV) than the thermal evaporation energy (~0.1 eV). The additional energy during laser ablation is utilized in recrystallization of thin films. The highly nonequilibrium nature of the pulsed laser evaporation/ablation process is an attractive means for the synthesis of stoichiometric thin films of various metal nitrides and oxides from the corresponding bulk targets. We recently reported the epitaxial growth of TiN films on Si(100) at substrate temperature as low as 500–600 °C by the pulsed laser deposition technique. In the previous studies, the laser deposited AIN films were found to contain amorphous or polycrystalline to textured microstructures. In this article, we report the formation of epitaxial AIN on Si(111) by PLD. Our results clearly indicate that smooth and epitaxial AIN films can be grown on Si(111) with \(c\) axis normal to the film surface at a temperature of 750 °C by pulsed laser ablation of stoichiometric AIN target. Although the lattice parameters of AIN and Si are significantly different from each other for a lattice matching epitaxy, we propose domain matching epitaxy as a possible mechanism for epitaxial growth of AIN on Si(111) substrates.

II. EXPERIMENT

The AIN films were deposited inside a stainless steel vacuum system evacuated by a turbomolecular pump to a base pressure of \(1 \times 10^{-7}\) Torr. Radiation from a KrF excimer laser (\(\lambda = 248 \text{ nm}, \tau = 25 \times 10^{-9} \text{ s}\)) was used to ablate the AIN target. The laser beam was focused through a UV optical window into the laser ablation chamber using a spherical lens with a 50 cm focal length. The stoichiometric hot pressed AIN target was ablated at an energy density ranging from 2 to 10 J/cm². During deposition, the background pressure rose to \(3 \times 10^{-5}\) Torr. The films were deposited at pulse repetition rate ranging from 10 to 30 Hz for 10–15 min. The ablated plume was ejected perpendicular to the target and deposited on to the substrates that were mounted 5 cm away and parallel to the target. Before deposition, the silicon (111) substrates were cleaned to remove the surface oxide layer using 5% HF solution. The substrates were heated radiatively and their temperature was measured by a thermocouple.
pressed directly onto the substrate surface. The films were deposited at three different substrate temperatures, i.e., 550, 650, and 720 °C. In order to study the role of nitrogen partial pressure on the quality of the AlN films, the depositions were carried out at nitrogen partial pressure of 5×10⁻⁴ Torr. In this study, all films were deposited in the range 2000–3000 Å.

AlN films were characterized by Fourier transform infrared spectroscopy (FTIR), Raman spectroscopy, and x-ray diffraction (θ–2θ and ω scans) using (Cu Kα radiation). Raman spectroscopy was carried out using green light (514.5 nm line) from Ar⁺ ion laser. The incident light was made grazing along the plane of the AlN film and the scattered light was collected in the direction normal to the substrate, i.e., along c axis of the AlN film. We have not used any polarization analyzer for the scattered light. The scattered light was dispersed in a one meter 1704 Spex monochromator with a resolution of 0.4 cm⁻¹ and the counts were taken for 1 min at each wavelength with a photomultiplier in photon counting mode. The nature of epitaxy in these films was studied using 200 kV Akashi-002B (Topcon) high resolution transmission electron microscope (TEM) with point-to-point resolution of 1.8 Å. The surface morphology was studied by scanning electron microscopy (SEM).

III. RESULTS AND DISCUSSION

The laser deposited thin films were characterized by FTIR and Raman spectroscopy to investigate the characteristics of infrared and Raman active modes in AlN. The AlN with wurtzite structure has nine optical branches. At long wavelengths, A₁ and E₁ are the infrared active and A₁, E₁, and E₂ are Raman active modes. Figure 1 shows the FTIR transmittance spectrum of laser deposited AlN film grown on Si(111) at a substrate temperature of 750 °C. This spectrum was obtained by computer subtraction of the Si(111) substrate background. The strong absorption peak at 665 cm⁻¹ is due to the transverse optical phonon modes of AlN. These phonon modes clearly show that the laser deposited films contain pure AlN phase. The films deposited at all substrate temperatures exhibited an IR spectrum characteristic of AlN. Figure 2(a) shows typical Raman spectrum of the polycrystalline AlN target used for the laser ablation. In this spectrum, A₁ [TO:610 cm⁻¹, LO:893 cm⁻¹], E₁[TO:667 cm⁻¹, LO:910 cm⁻¹] are the phonon modes of the AlN. These frequencies are in good agreement with the results reported previously. Figure 2(b) shows the Raman spectrum from an AlN film deposited on Si(111) at 750 °C. In our study, the phonon propagation vector was along the c axis of the film. In this configuration, the quasitransverse mixed A₁[TO:610 cm⁻¹, LO:893 cm⁻¹], E₁[TO:667 cm⁻¹, LO:910 cm⁻¹, 825 cm⁻¹], and E₂[655 cm⁻¹] modes are expected. The Raman spectrum from the AlN film clearly shows the above modes. It should be noted that the relative intensities of A₁, E₁, and E₂ modes are different for the film as compared to the target. This is attributed due to the texturing of the AlN film along the c axis normal to the substrate.

Detailed x-ray diffraction measurements (θ and ω scans) were carried out to study the crystalline properties of the laser deposited AlN films. Figure 3 shows “θ-2θ” angular scans of the AlN films deposited on Si(111) at three different growth temperatures 550 °C [Fig. 3(a)], 650 °C [Fig. 3(b)], and 750 °C [Fig. 3(c)] and laser energy density of 3 J/cm², pulse repetition rate of 15 Hz, and base pressure of 3×10⁻⁷ Torr. The diffraction patterns show expected Si(111) family of planes together with AlN (0002) and AlN (0004) reflections. No other AlN reflection is present indicating that the AlN films deposited at all temperatures are predominantly oriented along [0001] direction. The lattice constant c for these films is found to be 4.97 Å which is close to the litera-
FIG. 3. X-ray diffraction patterns of laser deposited AlN films on Si(111). AlN films were deposited at the base pressure of $3 \times 10^{-7}$ Torr and the substrate temperatures of (a) 550°C, (b) 650°C, and (c) 750°C.

ture value for the bulk AlN. It can also be seen that the integrated intensity of (0002) peak is low for the film deposited at 550°C and increases as a function of substrate temperature. The substantial increase in the integrated intensity of (0002) diffraction line corresponding to the AlN film deposited at 750°C indicates that the AlN basal plane, i.e., (0001) plane is parallel to the (111) plane of the Si substrate. It should be noted that the textured growth along the preferred direction for the films grown at lower temperatures is due to minimum surface energy of AlN(0002) relative to other planes. The x-ray rocking curve is a powerful technique to determine the epitaxial quality of the films. The distribution of crystals with definite orientation (mosaicity) with respect to the substrate normal is reflected in full width at half maximum of the rocking curve. The x-ray rocking curves were obtained for the films deposited at 550, 650, and 750°C. For the films deposited at 550°C, the width of the rocking curve was quite broad indicating poor alignment of the c axis with the substrate normal. The alignment of the film with respect to the substrate improves steadily with the increase of substrate temperature. The narrowest rocking curve obtained for AlN films grown on Si(111) substrates at 750°C was 1.15°. The ω resolution of the diffractometer is 0.3° as measured in the Si(111) reflection.

Figure 4(a) shows a selected area diffraction pattern from a cross-sectional specimen deposited at 750°C with base pressure of $3 \times 10^{-7}$ Torr. The spot diffraction pattern from AlN clearly shows that the film is single crystal. From the simulation [shown in Fig. 4(b)], the epitaxial nature of AlN on Si(111) is established. In the cross section, AlN[2110] is aligned with Si[001] axis. In the other two directions, we find that AlN[0110] || Si[422] and AlN[0001] || Si[111]. Similar epitaxial relationship has been reported for AlN films grown by reactive sputtering and chemical vapor deposition on Si(111) substrates.7,10 The characteristics of AlN film microstructure and the nature of AlN/Si(111) interface were investigated using high-resolution TEM. Figure 5(a) shows that the AlN/Si(111) interface is quite sharp without any
misfit \( f_d \) of 1.2\%. Such domain matching epitaxy provides a possible mechanism for epitaxial growth in this system with large lattice mismatch.

The effect of nitrogen partial pressure during laser deposition on the growth quality of AlN films was also investigated. It was found that the total integrated intensity of AlN(0002) x-ray diffraction peak decreases as a function of nitrogen partial pressure. The intensity of AlN(0002) diffraction peak dropped by factor of 3 while the rocking curve broadened from 1.1 to 1.9' for the film deposited at 750 °C and nitrogen partial pressure of \( 5 \times 10^{-4} \) Torr as compared to the film deposited at base pressure of \( 3 \times 10^{-7} \) Torr and the temperature of 750 °C. The pressure of the ambient gas significantly affects the reaction kinetics and particulate formation during the time of flight. It is believed that small clusters/particles are formed in the laser induced plasma plume generated in the high nitrogen partial pressure. This is primarily due to the fact that as the chamber pressure increases, the mean free path in background gas decreases significantly and the number of collisions within the laser induced plasma plume increases. The large number of collisions of the particles in the high background pressure are responsible for cluster formation. In fact, such small particles of <0.1 \( \mu \text{m} \) are observed by Norton et al. in laser ablated AlN films deposited in 30 mTorr pressure of nitrogen and these could be reduced further by lowering the nitrogen partial pressure during deposition. These clusters are deposited randomly on the substrate, causing degradation in epitaxial quality. The rapid quench rates experienced by the particles may lead to the formation of novel phases and metastable structures.

The influence of laser fluence and pulse repetition rate on the surface morphology of the AlN films was also investigated. The surface morphology of the films was studied by scanning electron microscopy. The SEM micrographs of the AlN films deposited at two different energy densities \( E = 3 \) and \( 10 \) J/cm\(^2\) are shown in Fig. 6. The film deposited at \( E = 3 \) J/cm\(^2\) is quite smooth with no particulates, as shown in Fig. 6(a). The growth rate at this energy density is found to be 0.22 Å/pulse. The film deposited at energy density of 10 J/cm\(^2\) as shown in Fig. 6(b) is found to contain particulates on the surface of the film, which is a common feature of the laser ablation at high energy density. The growth rate at this energy density is increased to 1.12 Å/pulse. These growth rates are extremely high for nitride deposition as compared to other deposition techniques. No significant effect of the pulse repetition rate up to 30 Hz on the film quality was observed, which indicates that the films of AlN can be grown at higher rates using the pulsed laser deposition technique.

IV. CONCLUSION

Thin films of AlN have been grown epitaxially on Si(111) substrate by pulsed laser ablation technique. The quality of the films was found to depend strongly on the laser fluence, substrate temperature, and nitrogen partial pressure during deposition. The x-ray diffraction studies revealed that the integrated intensity of AlN(0002) line increases as a function of substrate temperature and the corresponding...
FIG. 6. SEM micrographs of AlN films on Si(111) substrates, deposited at two different laser fluences (a) 3 J/cm² and (b) 10 J/cm².

rocking curve width decreases with lowering of nitrogen partial pressure and increase of substrate temperature. The FTIR and Raman spectroscopy results clearly showed the formation of high quality AlN phase. Using x-ray diffraction and high-resolution TEM, we have established the following epitaxial relationship AlN[0001]∥Si[111] and AlN[2110]∥Si[011]. We found that high quality AlN films can be deposited at a substrate temperature of 750 °C and a base pressure of 3×10⁻⁷ Torr in the absence of nitrogen.

ACKNOWLEDGMENTS

We acknowledge scientific contributions of Dr. S. Oktyabrsky and Dr. W. D. Fan of our group.