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Optimization of energy and fluence of N_2^+ ions in the conversion of Al_2O_3 surface into AlN at room temperature

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ABSTRACT

The work presents a systematic study of energetic N_2^+ ion interaction with the clean Al_2O_3 surface at room temperature. Energetic N_2^+ ions with energies ranging from 0.1 to 5 keV were bombarded onto the *c*-plane Al_2O_3 surface *in situ* in a UHV system equipped with X-ray Photoelectron Spectroscopy. Survey scans and core level spectra of Al(2p), O(1s), N(1s) were recorded as a function of ion fluence. Survey scans of XPS are used for the compositional analysis, while deconvoluted core level spectra are used to identify the evolution of the chemical bonding. Energetic dependence of N_2^+ ions occupying interstitial and substitutional sites in Al_2O_3 lattice are probed to follow the surface evolution. Results show that maximum thickness of surface is nitride by 5 keV N_2^+ ion with an optimal fluence of 1.5×10^{15} ions/cm^2. This modified surface can be used as a template for low defect III-nitrides growth, with enhanced lattice matching than on bare *c*-Al_2O_3.

1. Introduction

Inspite of a wide range of applications in optoelectronics and microelectronics devices, III-nitrides are still lacking in efficiency due to the inavailability of suitable lattice matched substrate. Sapphire remains one of the most used substrates despite of having a large lattice mismatch (∼13%) and thermal expansion mismatch (∼54%). In view of this pre-growth of buffer layers of AlN or GaN, use of surfactant, patterning of the substrate, etc. have been employed to improve the quality of the over-grown GaN films [1–3]. High quality GaN films can also be obtained by nitriding the sapphire substrate surface, by using nitrogen plasma or energetic ions before film growth, due to the relaxation of the interfacial free energy between the GaN and the interfacial AlN reaction layer, which also minimizes the lattice mismatch [4–9]. Though there are a several reports on the nitridation of Al_2O_3 by energetic nitrogen ions [10–17], a systematic energy and fluence dependent study related to the formation of AlN on Al_2O_3 has not been reported as yet, to the best of our knowledge. We have previously reported studies on the ion and Ga induced surface modification of GaAs and Si(1 1 1) at room temperature [18–22], and now investigated the energetic N_2^+ ion interaction with atomically clean Al_2O_3 (0 0 0 1) surface.

Nitrogen ion beam induced nitridation done in MBE systems can be more effective in obtaining better epitaxy film, since it can operate in a much better vacuum than that conventionally used by plasma processes. Using energetic ions can enable low temperature growth of single crystalline and smooth AlN layers, mitigating the ill-effects of the thermal expansion mismatches. Thus, the need to identify an optimal process that is compatible to MBE growth prompted us to undertake this work and understand the interfacial change during the nitridation of Al_2O_3 by medium energy N_2^+ ions. These experiments were performed in an ultra high vacuum (UHV) system, and probed *in situ* by X-ray Photoelectron Spectroscopy (XPS). Survey scans and core level spectral analysis are used to estimate the atomic composition, while core level spectra are deconvoluted to obtain information about the evolution of different oxidation states. We have optimized the energy and fluence of nitrogen ions for the formation of AlN on Al_2O_3 (0 0 0 1) surface.

The experiments were performed *in situ* in an UHV chamber working at base pressure of 5×10^{-10} Torr, equipped with X-ray Photoelectron Spectroscopy (PHI Model 1257). The details of the XPS system are given elsewhere [18]. A 20 mm × 20 mm, *c*-plane Al_2O_3 piece from a commercial wafer (0 0 0 1) was chemically cleaned before mounting it on the sample manipulator in the UHV

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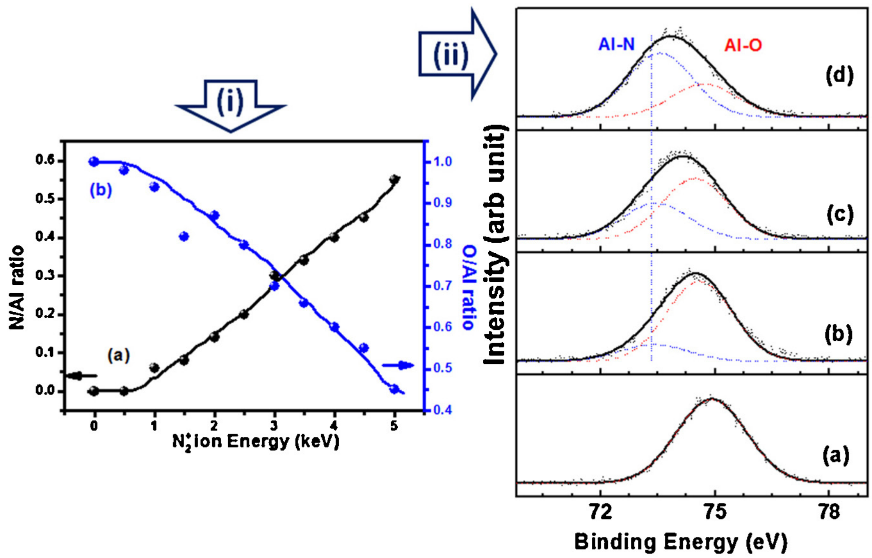

Fig. 1. (i) Shows change in N(1s)/Al(2p) and O(1s)/Al(2p) intensity ratio as the Al_2O_3 surface is bombarded by different energy N_2^+ ions. (ii) Shows the deconvoluted Al(2p) core level spectra, where (a), (b), (c) and (d) correspond to the clean Al_2O_3, 1 keV, 3 keV and 5 keV nitridation for N_2^+ ion fluence of 3×10^{13} ions/cm^2, respectively.

chamber, followed by *in situ* low energy (1 keV) Ar^+ ion bombardment to remove surface contaminants without affecting the crystal structure. Surface cleanness was ascertained by XPS survey scans where the absence of impurities and the presence of only the Al and O bonds corresponding to stoichiometric Al_2O_3 are seen. The resolution for the survey scan was 0.7 eV using pass energy of 100.0 eV, while for core levels it was 0.1 eV with the pass energy of 25.0 eV at 90% of the peak height. This cleaned surface was exposed to the N_2^+ ion bombardment using a sputter ion gun operating in the range of 100 eV to 5 keV rastered over a 10 mm × 10 mm area of the sample. The ion flux was calculated from the target current (converted to number of ions) measured on the sample during ion bombardment, divided by the raster surface area. The ion dose (fluence) was determined by multiplying the ion flux with exposure time. Survey scans and core level spectra of Al(2p), O(1s), N(1s) and C(1s) have been recorded after each nitridation step and deconvoluted into their respective Gaussian components to get the qualitative bonding information. Specific measures were taken to correct the accumulation of charge at the surface of insulating Al_2O_3 surface. We have used conducting carbon tape very proximal to X-rays to minimize the charging effect. However, the small shift in the core levels was corrected by taking graphitic carbon peak at 284.6 eV. In the first part of the experiments, we have exposed the clean Al_2O_3 (0 0 0 1) surface to different energetic N_2^+ ions of constant fluence, while in second part the clean Al_2O_3 surface was exposed to different N_2^+ ion fluence by keeping energy constant. The study enables us to find the optimal ion energy and fluence for effective Al_2O_3 (0 0 0 1) nitridation. Issues related to sputtering of material with energetic ions have also been taken care to insure only electronic transition induced effect, by keeping the energy up to 5 keV, above which sputtering effect can dominate.

2. Results and discussions

In the first part, we have exposed clean *c*-plane Al_2O_3 surface to N_2^+ ions of different energy at a constant fluence of 5×10^{14} ions/cm^2. The resultant N/Al and O/Al core-level XPS intensity ratio is plotted in Fig. 1(i). Curve (a) shows the change in N/Al ratio, while (b) shows the change in O/Al ratio, with varying N_2^+ ion energy. Figure shows that for N_2^+ ion energy up to 0.5 keV, N(1s) peak is not observed and the O/Al ratio remains constant, showing the requirement of a threshold energy for the formation of AlN by energetic N_2^+ ions. As the N_2^+ ion energy increases from 0.5 eV to 5 keV, a monotonic increase in the N/Al intensity ratio and a decrease in the O/Al ratio is observed, showing the conversion of top layers of Al_2O_3 surface into AlN. Fig. 1(ii) shows the deconvoluted normalized Al(2p) core level spectra, where the peaks at 73.5 eV and 74.7 eV are due to related to the Al–N and Al–O related state, respectively [21]. The figure shows the gradual conversion of the pure Al_2O_3 in Fig. 1(ii)a, to a dominant AlN form co-existing with Al_2O_3 in Fig. 1(ii)d, with increase in the N_2^+ ion energy. Thus Fig. 1 shows that as N_2^+ ion energy increases the overlayer conversion of Al_2O_3 into AlN increases and maximum conversion was found to be for 5 keV N_2^+ ions for constant ion fluence in the ion energy range studied.

After identifying the energy dependence for the conversion of Al_2O_3 in to AlN, we have performed experiments to investigate optimal fluence for the AlN formation for different energetic N_2^+ ions ranging from 0.1 to 5 keV. Fig. 2 plots the N/Al ratio, when the clean surface was exposed to 1 keV, 3 keV, 4 keV and 5 keV N_2^+ ions as a function of ion fluence ranging from 10^{13} to

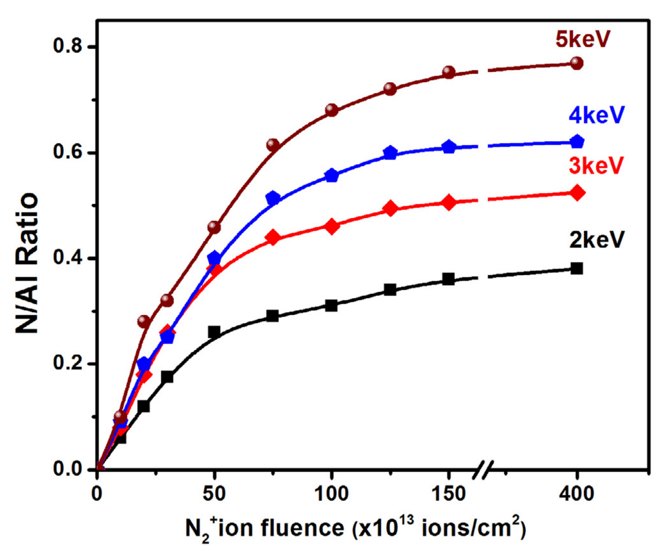

Fig. 2. Change in the N(1s)/Al(2p) intensity ratio for the Al_2O_3 surface bombarded by (a) 1 keV, (b) 3 keV, (c) 4 keV and (d) 5 keV N_2^+ ions, as a function of fluence.