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Photoemission Study of Aluminum Oxynitride/Si(100) Heterostructures — Chemical Bonding Features and Energy Band Lineup —

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1. Introduction

Amorphous aluminum oxide shows several properties favorable for a gate dielectric on Si such as large energy bandgap, thermodynamic stability against phase transition, crystallization and reaction with Si although having a dielectric constant only ~2.5 times larger than SiO_2. In that regard, the practical use of Al_2O_3 and aluminates as alternative gate dielectrics has been intensively investigated as well as silicates with transition metal atoms such as Zr and Hf for the CMOS technology beyond the 70nm node and its feasibility has so far been demonstrated [1-4]. However, the high negative fixed charge, typically of the order of $10^{12}cm^{-2}$, in amorphous Al_2O_3 and consequently reduced mobility remain critical issues. In addition, for Al_2O_3 films grown by an atomic-layer controlled CVD technique the significant dopant diffusion from the poly-Si gate has been reported [5]. To overcome this problem and to suppress undesirable oxidation of Si during CVD and post annealing, the addition of nitrogen atoms into Al_2O_3 is a feasible way on the analogy of the replacement of pure SiO_2 with silicon oxynitride.

In this work, for aluminum oxynitirde (AlO_x:N) thin films prepared on Si(100) with a combination of CVD and NH_3 annealing in a layer-by-layer fashion, we have examined the chemical bonding features in the film and at AlO_x:N/Si(100) interfaces and measured the energy bandgap of ultrathin AlO_x:N and the valence band offset at the interface to determine energy band lineup between AlO_x:N and Si(100) by XPS measurements.

2. Experimental

AlO_x:N films were deposited on HF-last Si(100) in a UHV-compatible multiple chamber system by repeating nanometer CVD using a gas mixture of N_2O and AlH_3 stabilized with $N(CH_3)_2C_2H_5$ and rapid thermal annealing in ambient NH_3. After introducing a pre-cleaned Si wafer to a load-locked reaction chamber, the reaction chamber was evacuated down to ~$1x10^{-8}$ Torr with a turbo molecular pump. The wafer heating in the cold wall reaction chamber was preformed by infrared irradiation through a quartz window from a halogen lamp. The substrate temperature and the total gas pressure during deposition were maintained 300°C and 0.6Torr, respectively, and for NH_3 anneal 700°C and 5 Torr, respectively. In some cases, O_2 anneal was carried out at 700°C under 100 Torr after film formation. AFM images and cross-sectional TEM observations confirm the formation of a very uniform film and an atomically-flat interface. For high-resolution XPS measurements, monochromatized AlKα radiation was utilized.

3. Results and Discussion

No carbon incorporation into AlO_x:N films was detected by angle-resolved XPS measurements as expected in the use of AlH_3 with alkylamine as a thermally-stable ligand. Si2p spectra from AlO_x:N thin films formed on Si(100) show chemicall-shifted distinct signals at ~102eV independent of the film thickness as indicated in Fig. 1. The Si2p spectra normalized by the signals originating from the Si substrate are almost identical to the spectrum obtained for 1.0nm-thick silicon nitride fromed on Si(100) by a direct nitridation in ambient NH_3 at 700°C. The formaition of the 1.0nm-thick SiN_x interfacial layer is also confirmed from the photoelectron take-off angle dependence of Si2p and N1s spectra. NH_3 annealing in the early stages of the layer-by-layer process we used is responsible for such a self-limited, namely diffusion-liminted, formation of the interfacial SiN_x layer. By deconvoluting N1s spectra using the reference spectrum taken for the directly-nitirided Si, we found that the component due to nitrogen atoms into AlO_x:N layer is separated by ~1.2eV from the peak due to the interfacial SiN_x accompanied with a higher oxidized surface component as shown in Fig. 2. Considering the fact that the top electronic states of these nitrides are formed by non-bonding N2p states, the observed energy separation (1.2eV) corresponds to the valence band offset between AlO_x:N and SiN_x as directly confirmed in the analysis of the valence band spectra. The nitrogen content in the AlO_x:N layer is increased with the number of the layer-by-layer cycles and therefore with film thickness; the average concentration is 4.2at.% for the 3.3 nm-thick film and 21.4 at.% for the10nm-thick film. From the specral deconvolution of Al2p and O1s using the corresponding reference spectra of thermally-grown pure Al_2O_3, the observed spectral broadening can not be interpreted fully by the formation of Al-N and N-O bonds but by additionally the contribution of a positively-charged component is suggested for 10% of the total signals. The charged component might be attributed to a hole-trapped unit in which an Al atom is coordinated with six O atoms. The energy bandgap values for the oxide (or nitride) films were determined from the threshold energy of the energy-loss spectrum for O1s (N1s) photoelectrons as shown in Figs. 3 and 4. The energy bandgap of the AlO_x:N films is decreased slightly with increasing nitrogen content and increased slightly by O_2 annealing at 700°C. Such a weak compositional dependence of the energy bandgap and a significant decrease from the value of pure Al_2O_3 (~7eV [6]) are attributable to the band edge states mainly derived from N2p states. From the result of Fig. 4, the bandgap value for the interfacial SiN_x layer is estimated to be ~5.5eV which is obtained for directly-nitirided Si showing the almost identical Si2p (see Fig. 1). Figure 5 shows the valence band spectra measured for 4.0nm-thick AlO_x:N/1.0nm-thick SiN_x/Si(100) before and after O_2 anneal at 700°C and the result that the spectrum after the O_2 anneal was deconvoluted into three components due to the constituent materials by using the measured valence band spectra for Si(100) and the directly-nitrided Si. In the spectral deconvolution, the binding energy of each valence band spectrum was calibrated by the energy position of core-line peaks such as Al2p, Si2p, and O1s. Obviously, no significant change in the valence band spectrum between the AlO_x:N/SiN_x/Si(100) heterostructures before and after the O_2 anneal is observable. Since the spectrum of the ultrathin SiN_x layer is quite similar to that of CVD Si_3N_4, the valence band edge of the ulrathin SiN_x layer was determined from the onset of the Si_3N_4 valence band spectrum as indicated in Fig. 6. Note that the energy separation between the valence band tops of AlO_x:N and SiN_x is determined to be 1.2eV as suggested in the N1s chemical shift (see Fig. 2). Considering the band-gap values and the valence-

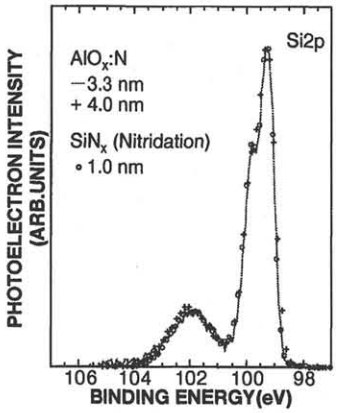

Fig. 1 Si2p spectra for 4.0nm-thick and 3.3nm-thick AlO_x:N films on Si(100). The spectra 1.0nm-thick SiN_x on Si(100) prepared by 700°C nitridation in ambient NH_3 is also shown as a reference.

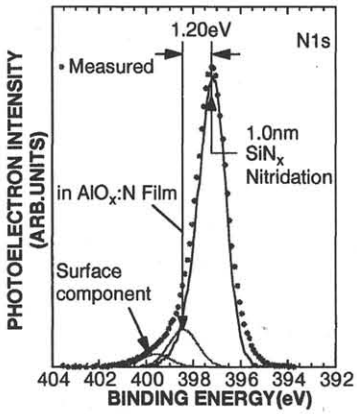

Fig. 2 N1s spectrum for the 4.0 nm-thick AlO_x:N film and deconvoluted spectra.

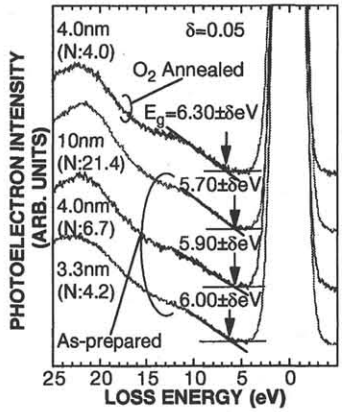

Fig. 3 Energy loss spectra of O1s for AlO_x:N films before and after O_2 annealing. The value in each set of parentheses denotes the nitrogen content in the film in the unit of at.%.

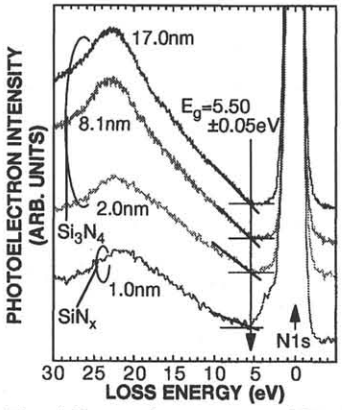

Fig. 4 Energy loss spectra of N1s for CVD Si_3N_4 and 1.0nm-thick SiN_x formed by direct nitridation in ambient NH_3.

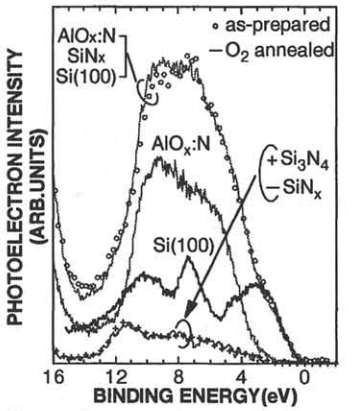

Fig. 5 Valence band spectra for AlO_x:N(4nm)/SiN_x(1nm)/Si(100) before and after O_2 annealing and deconvoluted spectra for annealing sample. The valence band spectrum of CVD Si_3N_4 is also shown as a reference.

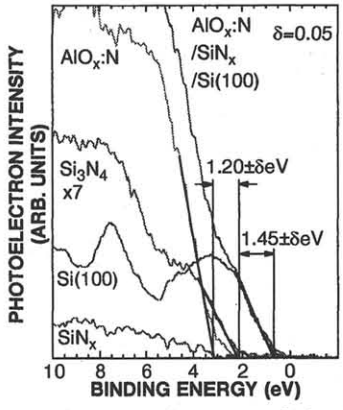

Fig. 6 Enlarged spectra of Fig. 5 to determine the valence band top for each of the components.

band lineups, the energy band profile for the O_2-annealed heterostructure was obtained as represented in Fig. 7.

4. Conclusions

The formation of AlO_x:N films on Si(100) from a combination of LPCVD using N_2O+AlH_3:N$(CH_3)_2C_2H_5$ and NH_3 annealing in a layer-by-layer fashion has been demonstrated. Due to the nitridation of Si(100) during the NH_3 anneal step, a 1.0nm- thick SiN_x interfacial layer is formed. The energy band gap and valence band edge of AlO_x:N are determined by electronic states derived from N atoms. From the viewpoint of the potential barrier height for carriers, the energy band alignment between AlO_x:N and Si(100) is roughly symmetric with respect to the experimental uncertainty of ~0.1eV.

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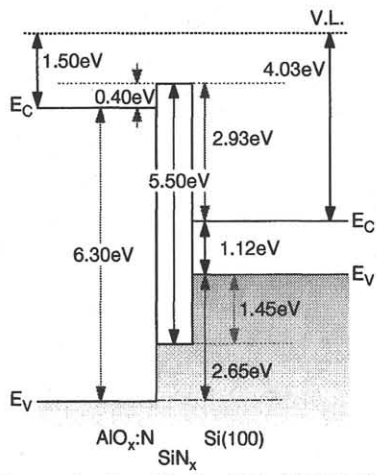

Fig. 7 Energy band profile for AlO_x:N/SiN_x/Si(100).

References

[1] D. A. Buchanan et al ., IEEE Int. Electron Device Meet. Tech Dig. (2000) p. 223.

[2] K. Torii et al ., Proc . Int. Workshop on Gate Insulator (2001) p. 230.

[3] E. P. Gusev et al ., IEEE Int. Electron Device Meet. Tech Dig. (2001) p. 451.

[4] L. Manchanda et al ., Int. Workshop on Gate Insulator (2001) p. 56.

[5] J. Lee et al., IEEE Int. Electron Device Meet. Tech Dig. (2000) p. 645.

[6] S. Miyazaki, J. Vac. Sci. Technol. B 19 (2001) 2212.