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Effect of Nitrogen Annealing on the Electrical Properties of Ultrathin Crystalline γ-Al_2O_3 High-κ Dielectric Films Deposited on Si(111) Substrates

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1. Introduction:

The decrease of device dimensions has led to the need for alternative, high dielectric constant (κ) oxides to replace silicon dioxide as gate dielectric in CMOS devices.[1] As a high-k gate dielectric ultrathin crystalline γ-Al_2O_3 has achieved much attention due to its excellent electrical properties and thermal stability, higher barrier height, lower oxygen diffusion than that of HfO_2 and ZrO_2. Nitrogen incorporation into conventional SiO_2 or oxynitrides has been demonstrated to successfully lower leakage current, increase dielectric constant, to reduce flat band voltage (V_{fb}) and suppress boron penetration.[2] The fabrication and electrical characterization of ultrathin γ-Al_2O_3 dielectric films has been reported.[3] In this paper we report the incorporation of the nitrogen atoms into the ultrathin crystalline γ-Al_2O_3 films by annealing and their effect on the electrical properties.

2. Experimental:

Crystalline γ-Al_2O_3 films were fabricated by mixed source molecular beam epitaxy (MBE), aluminium as solid source and N_2O as gas source. All samples were deposited at 750°C substrate temperature. γ-Al_2O_3 films were fabricated in a two step growth process. Details of the film preparations were described elsewhere.[4,5] Samples were then annealed at different temperatures (300°C- 700°C) for 30 min. During annealing N_2 gas flowed through the chamber with a flow rate of 3 lit / min. Chemical compositions of these films were studied by XPS measurement. Finally a layer of Al (thickness 0.5 μm) were deposited on the films and back surface of the substrate by thermal evaporation and patterned for electrode by photolithography. Electrical measurements were performed by HP4140A pico-ampere meter and HP4192B semiconductor parameter analyzer.

3. Results and discussions:

XPS measurements were carried out to investigate the effect of N_2–annealing on the chemical composition of the ultrathin crystalline γ-Al_2O_3 films. Figure 1 shows a set of XPS spectra of ultrathin crystalline γ-Al_2O_3 films, as deposited and annealed at different temperatures. Samples annealed up to temperature 500°C, no detectable nitrogen peaks (N1s) were observed but when the annealing temperature was increased, N1s peak at a binding energy of 399 eV was observed at 600°C and 700°C. It reveals that nitrogen atoms incorporated into γ-Al_2O_3 films during the annealing in the nitrogen atmosphere. Figure 2 shows the dielectric breakdown field of the as deposited samples and annealed at 600°C as a function of electrode area. It was observed that the breakdown field increased after annealing. The breakdown field varies with the electrode area and as the electrode area increases the breakdown field decreases. It is a common phenomenon because as the area increases the defect density increases as a result the electrical property decreases. But the rate of decrease of breakdown field was smaller in the case of annealed samples compared with the as deposited samples. The leakage current density decreases about 3 order after annealing as illustrated in the Fig. 3. It reveals that the defect density decreases after annealing and the film quality improves i.e., crystal defects etc., decrease after annealing. Figure 4 illustrates the conventional capacitance-voltage characteristics of as deposited and annealed 3.3-nm-thick γ-Al_2O_3 films. After annealing the hysteresis in the capacitance-voltage characteristics was decreased. Before annealing the hysteresis was observed 42 mV whereas hysteresis after annealing was 16 mV. This hysteresis was observed due to the carrier injection into the ultrathin films.[3] Also the flat band voltage shift was decreased after annealing as illustrated in Fig. 4. Fixed oxide charge density of the γ-Al_2O_3 thin films was measured and negative fixed charge was observed. The Fixed charge density of the as deposited samples was estimated about 1×10^{13} cm^{-2} and for the annealed samples the value of fixed charge density was $1\text{-}5 \times 10^{12}$ cm^{-2}. The origin of this fixed charge is the atomic/electronic level defects.[6] As Al is a group-III element, may be a group V element (nitrogen) can neutralize the charged electronic state and reduce the fixed charge density.[7]

4. Conclusions:

Incorporation of nitrogen atom into the ultrathin γ-Al_2O_3 during annealing in the nitrogen atmosphere was confirmed in this study. Improvement in the electrical properties was observed after annealing in the nitrogen atmosphere. These improvements are attributed to nitrogen incorporation into ultrathin γ-Al_2O_3 high-k dielectric by annealing in the nitrogen atmosphere.

Acknowledgments

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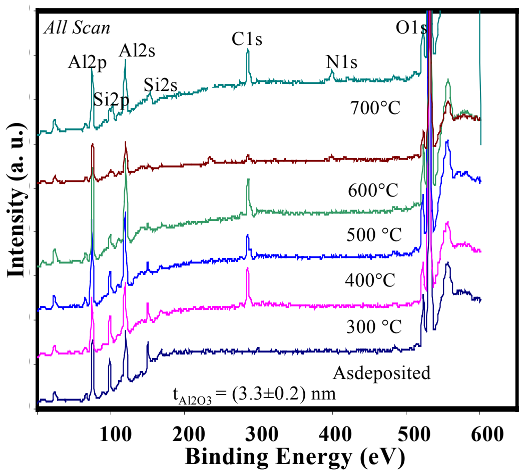

Figure 1. XPS spectra of as deposited and annealed crystalline γ-Al_2O_3 deposited on n-Si (111) substrate. Nitrogen 1s peak was observed at 399 eV for samples annealed at temperature 600 °C and over.

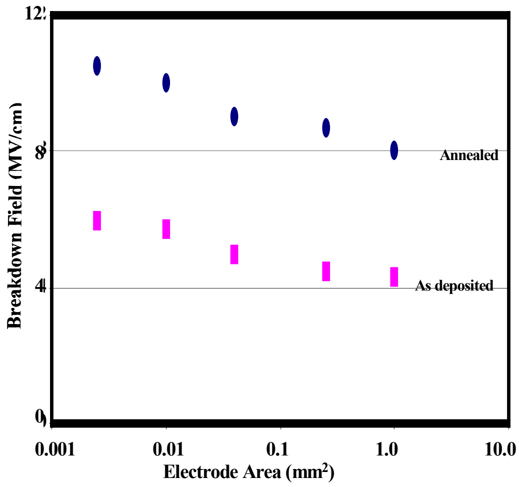

Figure 2. Dielectric breakdown field as a function of electrode area. Dielectric breakdown field increases after annealing.

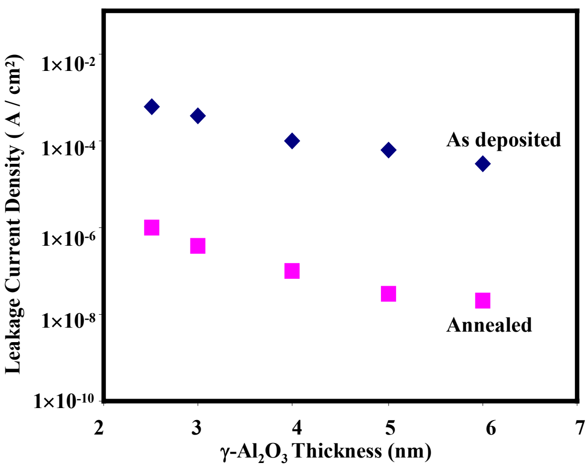

Figure 3. Leakage current density at an applied field of 3 MV/cm as a function of γ-Al_2O_3 thickness. Compared with the as deposited samples, the annealed samples show 3 order lower leakage current density.

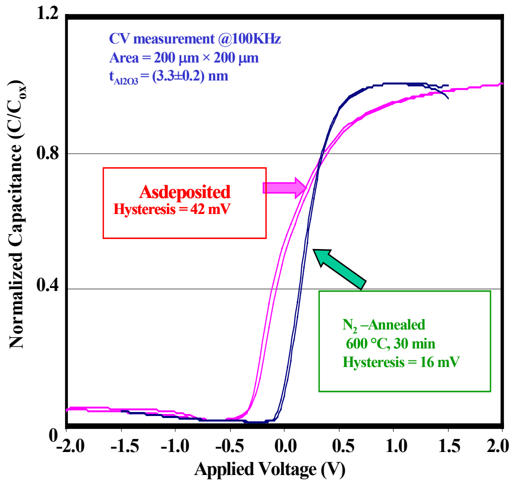

Figure 4. Hysteresis of capacitance-voltage characteristics of 3.3-nm-thick γ-Al_2O_3 deposited on n-Si (111) substrate. Hysteresis and flat band voltage shift decrease after annealing.