Electron Cyclotron Resonance Plasma-Assisted Atomic Layer Deposition of Amorphous Al₂O₃ Thin Films

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Abstract Without extra heating, Al₂O₃ thin films were deposited on a hydrogen-terminated Si substrate etched in hydrofluoric acid by using a self-built electron cyclotron resonance (ECR) plasma-assisted atomic layer deposition (ALD) device with Al(CH₃)₃ (trimethylaluminum; TMA) and O₂ used as precursor and oxidant, respectively. During the deposition process, Ar was introduced as a carrier and purging gas. The chemical composition and microstructure of the as-deposited Al₂O₃ films were characterized by using X-ray diffraction (XRD), an X-ray photoelectric spectroscope (XPS), a scanning electron microscope (SEM), an atomic force microscope (AFM) and a high-resolution transmission electron microscope (HRTEM). It achieved a growth rate of 0.24 nm/cycle, which is much higher than that deposited by thermal ALD. It was found that the smooth surface thin film was amorphous alumina, and an interfacial layer formed with a thickness of ca. 2 nm was observed between the Al₂O₃ film and substrate Si by HRTEM. We conclude that ECR plasma-assisted ALD can grow Al₂O₃ films with an excellent quality at a high growth rate at ambient temperature.

Keywords: ECR, ALD, Al₂O₃ thin film, TMA, HRTEM

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1 Introduction

Al₂O₃ thin films have attracted much attention due to their potential applications in diverse areas. For example, they can be used as passivating and protecting materials that may serve as gas diffusion barriers in food packaging and reducing the escape of CO₂ from pressurized soda containers. In microelectronics, Al₂O₃ thin films have been regarded as high-k materials to replace SiO₂ layers for gate dielectrics in devices such as in dynamic random access memory (DRAM) and metal-oxide-semiconductor field-effect transistors (MOSFETs) due to their excellent dielectric properties, good adhesion to many surfaces and thermal and chemical stability. So the growth of Al₂O₃ thin films is widely investigated and many methods are utilized to prepare Al₂O₃ thin films, such as metal organic chemical vapor deposition (MOCVD), molecular beam epitaxy (MBE), and atomic layer deposition (ALD). Among these techniques, the ALD process is the most prominent one due to its excellent uniformity, conformity and thickness control of the deposited thin films in the nanometer range.

Conventional ALD is thermal ALD, where the chemical reaction depends on the substrate temperature. For this reason a quite high substrate temperature (> 300 °C) is demanded in thermal ALD, which greatly limits the applications in the field of flexible electronics involving temperature-sensitive organic materials. So a new variant of ALD technology, a plasma exposure during the ALD cycle, has been explored, which is expected to provide even more benefits to the ALD process, such as a lower deposition temperature, higher quality films and an increased growth rate. This is so-called plasma-assisted ALD, where the substrate is exposed to the different species presented in the plasma. Then the reactive species, predominantly radicals, react with the surface groups created during the preceding precursor exposure, which leads to the reduction or oxidation of the chemisorbed precursor, and the creation of new surface groups and film formation. Since the chemical activity of radical species is ignited in the gas phase in plasma-assisted ALD, the process depends less on the thermal temperature of the substrate surface. This facilitates the deposition processing at lower temperatures, even at room temperature, and improves the material properties compared to those obtained through thermal ALD.

Since electron cyclotron resonance (ECR) plasma can demonstrate a high ionization degree with a high
density of electrons and ions compared to other plasma sources, it is expected that ECR-assisted ALD can be used to prepare a unique $\text{Al}_2\text{O}_3$ thin film. In this article, we present a homebuilt ECR plasma-assisted ALD process to prepare $\text{Al}_2\text{O}_3$ thin films without extra heating and with $\text{Al(CH}_3)_3$ (TMA) and $\text{O}_2$ plasma as precursor and oxidant, respectively.

2 Experiment

A schematic diagram of the ECR plasma-assisted ALD system is shown in Fig. 1, which consists of coils for the magnetic field, a plasma generation system, a stainless steel vacuum chamber, and a pumping system. The chamber is divided into a plasma generation source chamber and a deposition chamber. The 2.45 GHz microwave is transmitted through the rectangle waveguide and the quartz window into the plasma chamber. This is a typical remote plasma system with the substrate at a distance of $\sim10$ cm downstream from the plasma source, and it is beneficial to the radical deposition process.

$\text{Al}_2\text{O}_3$ films were grown on the p-type Si substrate (5 cm×5 cm) at room temperature with TMA and $\text{O}_2$ as precursor and oxidant, respectively. Prior to deposition, Si substrates were cleaned in hydrofluoric acid to remove the native SiO$_2$ layer and to produce the hydrogen-terminated Si surface. A TMA precursor and $\text{O}_2$ were alternately purged into the chamber by the sequential injection of TMA pulses and $\text{O}_2$ pulses, and an Ar pulse was intervened between the two pulses to purge the chamber. The flow rate of the TMA was controlled by altering the pressure of the bubbler using a needle valve. Ar, delivered at a constant flow rate of 20 sccm, served as the carrier gas. The deposition cycles consisted of 3-s TMA pulse/10-s Ar purge/3-s $\text{O}_2$ pulse/10-s Ar purge. The deposition cycles were varied from 50 to 300 based on the measurement requirements.

The growth rate was divided from the film thicknesses measured by spectroscopic ellipsometer (HORIBA, Jobin Yvon, France) by the deposition cycles. The morphologies of the $\text{Al}_2\text{O}_3$ films were characterized by using SEM (S-4800, Hitachi) and AFM (Dektak 150, Vecoo, USA). The chemical structure, the crystalline status of the $\text{Al}_2\text{O}_3$ films and the interfaces were investigated by using an XPS (MKII, VG, England) and XRD (Bruker-axs, D8 Advance), respectively. The cross-sectional image obtained from the HRTEM (JEOL, JEM 2010 FEF UHR) was used to characterize the microstructure and interfacial layer.

3 Results and discussion

Fig. 2 shows the variation in the $\text{Al}_2\text{O}_3$ film thickness with the number of cycles. One can see that the thickness of the $\text{Al}_2\text{O}_3$ films is precisely proportional to the number of cycles. It means that the film was grown in the ALD mode. The 0.24 nm /cycle growth rate, deduced by dividing the film thickness by the number of growth cycles, is remarkably higher than that deposited by thermal ALD (ca. 0.12$\sim$0.13 nm/cycle [12]). The possible reason is the higher reactivity of the oxygen radicals generated by the plasma attacking TMA aggressively, which then react completely with Al-$\text{CH}_3$ and grow film on the substrate [13]. In Fig. 2 the plot of film thickness versus process cycles has no zero crossing, which means the deposition model in plasma-assisted ALD is different from thermal-ALD, where a typical phenomenon passes zero [14].

Fig. 2 $\text{Al}_2\text{O}_3$ film thickness vs. number of growth cycles in ECR plasma-assisted ALD

The surface morphologies of the $\text{Al}_2\text{O}_3$ film deposited in 300 cycles revealed by the SEM and the AFM are shown in Fig. 3. It shows that the $\text{Al}_2\text{O}_3$ film has excellent conformity and a large area of uniformity. The root mean square (RMS) roughness of the surface is only about 0.4 nm, smaller compared to films deposited by other methods such as pulse laser deposition [15], chemical vapour deposition [16], and MBE [17]. This indicates that the ECR plasma-assisted ALD method is very suitable for the preparation of high-$k$ materials with excellent conformity and a large-area of uniformity.
That there is no appearance of a crystalline diffraction peak of Al$_2$O$_3$ in the XRD analysis suggests that the as-deposited Al$_2$O$_3$ film at such a low temperature is in an amorphous state.$^{[18]}$ Generally, Al$_2$O$_3$ films deposited at low substrate temperatures (usually < 400°C) demonstrate a homogeneously amorphous structure.$^{[19]}$ The formation of crystalline Al$_2$O$_3$ can be achieved at a high growth temperature, or with post-annealing treatment of amorphous Al$_2$O$_3$ (typically > 800°C).

Fig. 4(a) shows the XPS spectra of the Al$_2$O$_3$ films deposited in 300 cycles. All binding energies were referenced to the C1s core peak at 285 eV. Based on the data in the National Institute of Standards and Technology (NIST) XPS database, the appearance of Al2s at 119.2 eV and Al2p at 74.4 eV confirms the formation of Al$_2$O$_3$.$^{[19]}$ The Al2p and O1s core spectra are shown in Fig. 4(b) and (c), respectively. The Al2p spectrum fitted into one peak is Al2p (Al-O bond) in Al$_2$O$_3$ with the binding energy at about 74.4 eV.$^{[20]}$ The binding energy of 72.8 eV corresponding to the Al-Al bond is not observed. This suggests that the as-deposited Al$_2$O$_3$ film is not oxygen-deficient. The stoichiometric ratio of oxygen to aluminum (O/Al) of the film is derived as 1.62 by calculating the peak areas of the Al2p and O1s spectra, which indicates that the as-deposited Al$_2$O$_3$ film is oxygen-rich.

In addition, the diffusion of O atoms from as-deposited alumina also possibly causes the oxidization of the Si substrate.$^{[21]}$ It is only when a sufficient thickness of Al$_2$O$_3$ has suppressed the diffusion of oxygen radicals to the Si surface, can the oxidization be stopped in the
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growth process.

Fig. 5  Cross-sectional HRTEM images of the as-deposited Al$_2$O$_3$ films: (a) bar scale 100 nm; (b) bar scale 20 nm (color online)

4 Conclusion

Al$_2$O$_3$ thin films were deposited on an HF (hydrogen fluoride)-cleaned Si substrate by using a homebuilt ECR plasma-assisted ALD setup with TMA and oxygen gas used as precursor and oxidant, respectively. The results showed that the growth rate was ca. 0.24 nm/cycle, which is much higher than that with deposition by thermal-ALD. It is noticed that the thin film was amorphous Al$_2$O$_3$ with a quite smooth and uniform surface. With XPS analysis, the as-deposited Al$_2$O$_3$ films were confirmed to be oxygen-rich. An interfacial layer with a thickness of about 2 nm was observed in the Al$_2$O$_3$ films deposited in 300 cycles. We assumed that this interfacial layer was composed largely of SiO$_x$ based on the HRTEM image. In summary, we conclude that the ECR plasma-assisted ALD process might be an efficient alternative for the deposition of ultra-thin and excellent quality Al$_2$O$_3$ films at room temperature.

References


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