Enhancing the thermal conductivity of polymer-assisted deposited Al_2O_3 film by nitrogen doping*

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Polymer-assisted deposition technique has been used to deposit Al_2O_3 and N-doped Al_2O_3 (AlON) thin films on Si(100) substrates. The chemical compositions, crystallinity, and thermal conductivity of the as-grown films have been characterized by X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), and 3-omega method, respectively. Amorphous and polycrystalline Al_2O_3 and AlON thin films have been formed at 700 °C and 1000 °C. The thermal conductivity results indicated that the effect of nitrogen doping on the thermal conductivity is determined by the competition of the increase of Al–N bonding and the suppression of crystallinity. A 67% enhancement in thermal conductivity has been achieved for the samples grown at 700 °C, demonstrating that the nitrogen doping is an effective way to improve the thermal performance of polymer-assisted-deposited Al_2O_3 thin films at a relatively low growth temperature.

Keywords: nitrogen-doped Al_2O_3 thin film, thermal conductivity, polymer-assisted deposition

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1. Introduction

Negative charged aluminum oxide (Al_2O_3) dielectric thin film has been widely used as a high-k gate oxide in metal–oxide–semiconductor (MOS) structures and a dielectric layer in embedded capacitors.[1−4] Moreover, Al_2O_3 thin films have shown potential applications in optoelectronic devices and solar cells.[5−7] On the other hand, for optimizing the interface states, restraining the boron diffusion, and increasing the crystallization temperatures of oxide films, nitrogen-doped (N-doped) oxide films (HfO_2, HfSiO, ZrO_2, Al_2O_3) have been investigated to improve the performance of metal–insulator–semiconductor (MIS) structures.[8−12] Among them, the nitrogen-doped Al_2O_3 (AlON) thin film draws much attention due to its potential to combine the electrical and thermal advantages of AlN and Al_2O_3 thin films for possible applications as the dielectric layer in electronic devices.[13−17] Compared to the conventional Al_2O_3 insulator layer, the AlON thin film shows better barrier effect on the interdiffusion between the oxide layer and the silicon substrate, lower interface states, and nearly the same high dielectric constant (ε_r ∼8.9).[16−18] Although the benefits of AlON thin film to the electrical performance of microelectronic devices have been widely reported,[16−19] its influence on the thermal performance has not been fully explored as to the best of our knowledge. With the development of integrated circuit technology, the power densities of micro-electronic devices rapidly increase, which makes the thermal management become an important topic. To improve the thermal performance of a device, the thermal properties of each part of the device should be systematically investigated. As it has been reported, with high thermal conductive dielectric layers, the thermal performance of ultra-large scale integration (ULSI) would be improved, and an obvious decrease of the working temperature of the MOS device could be achieved.[20,21] Thus, it is valuable to study the thermal performance of new dielectric materials in the form of thin film, such as AlON thin films.

Al_2O_3 thin films can be fabricated on silicon substrates by many methods: chemical vapor deposition (CVD),[1] atomic layer deposition (ALD),[3−6] ion-assisted electron beam evaporation (IAEBE),[7] magnetron sputtering,[2,22] and

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chemical solution deposition (CSD) technique.[23] And magnetron sputtering,[16,19] chemical vapor deposition,[17,24] plasma nitridation, and rapid thermal nitridation of Al_2O_3 thin films[25,26] have been used to fabricate AlON thin films. Among those techniques, the CSD technique offers the advantages of low cost and easy set-up. However, in the traditional CSD techniques such as the typical sol–gel method, it is still challenging to well control the hydrolysis of metal alkoxides, which may affect the stability and controllability of the precursor solutions. A polymer-assisted deposition (PAD) technique has been developed to deposit many kinds of films with excellent properties.[27−30] This technique distinguishes itself from the conventional CSD techniques by using water soluble polymers to bind metal ions, which avoids the hydrolysis process and prevents the premature precipitation and formation of metal–oxide oligomers. Thus, it shows not only the advantages of the sol–gel technique, but also much better stability and controllability for both the solutions and the fabrication process.

In this paper, we report our studies on the thermal conductivities of Al_2O_3 and AlON thin films fabricated by the PAD technique. Both Al_2O_3 and AlON thin films were deposited on Si(100) substrates, and the compositions of Al_2O_3 and AlON thin films were confirmed by X-ray photoelectron spectroscopy (XPS). X-ray diffraction (XRD) was applied to study the crystallinity of the films. The thermal conductivities of Al_2O_3 and AlON thin films were investigated by 3-omega method. The results demonstrated that the nitrogen doping would suppress the crystallization and increase the thermal conductivities of Al_2O_3 thin films.

2. Experimental details

To deposit Al_2O_3 and AlON thin films, the Al precursor solution was first prepared as described previously.[30] That is, 10-g polyethyleneimine (PEI), 5-mL 48% hydrofluoric acid (HF) solution, and 10-g $5H_2O{\cdot}Al(NO_3)_3$ were dissolved in 80-mL deionized water, then it was filtrated to 40-mL Al precursor solution. Prior to deposition, silicon substrates were cleaned by acetone, alcohol, and deionized water sequentially, then etched in 10% HF solution for 3 min to remove the native silicon oxide and rinsed in deionized water and alcohol, finally blowing dried with nitrogen gas. The Al precursor solution was then spin-coated on the as-cleaned Si(100) substrates at 5000 rpm for 30 s. The films were heat treated in forming gas (400 sccm of 6% H_2 and 94% N_2) at 510 °C for 2 h to de-polymerize the polymer. Then the films were annealed at a certain temperature for 2 h in air to form the Al_2O_3 thin films or in wet ammonia gas (300 sccm) to form AlON thin films. Two annealing temperature, i.e., 700 °C and 1000 °C, have been studied in this paper.

The chemical compositions and the chemical bonding states of the films were examined by XPS, and the thicknesses of the as-grown Al_2O_3 and AlON thin films were checked by cross-sectional scanning electron microscope (SEM). The crystal structures of the as-deposited films were checked by XRD using Cu $K\alpha$ radiation (λ = 1.54178 Å, DX1000, China, 1 Å=0.1 nm). The cross-plane thermal conductivity from 80 K to 300 K was tested by using a home-made 3-omega system. The schematic diagram of the 3-omega measurement system is shown in Fig. 1. The principle of the measurement is given in the literatures.[31,32] A digital lock-in amplifier SR830 (Stanford Research System) was used as a voltage source and a third harmonic voltage detector. A bridge circuit was set up to differentially subtract the first harmonic voltage and acquire the nonequilibrium third harmonic voltage. A current meter was connected to the sample in series to measure the current. And a Ti/Au metal line, 10 μm in width and 1 mm in length, deposited on the surface of the as-grown sample by lithography and magnetron sputtering, served simultaneously as the heater and the thermocouple. The temperature coefficient of the metal line was measured before measuring the thermal conductivity. The measurements were conducted in a vacuum cryostat system (Janis VPF-500).

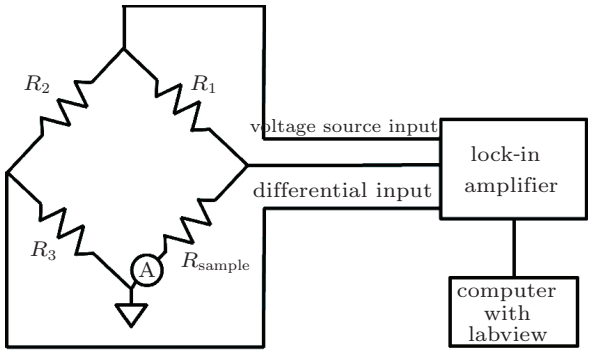


Fig. 1. Schematic diagram of the home-made 3-omega measurement system.

3. Results and discussion

Figure 2 shows the cross-sectional SEM images of Al_2O_3 and AlON thin films deposited at 700 °C. It is indicated that the films are continuous with smooth surfaces. The thicknesses of both films are approximately 210 nm.

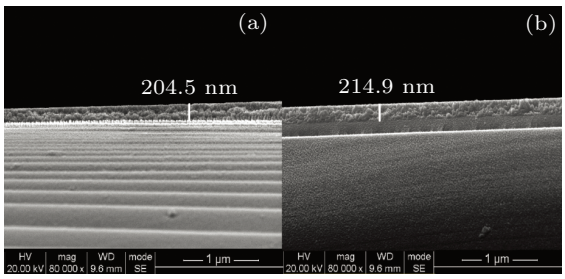


Fig. 2. Cross-sectional SEM images of (a) Al_2O_3 and (b) AlON thin films.

Table 1. Chemical compositions of Al_2O_3 and AlON films.

Sample		Al/at%	O/at%	N/at%	Si/at%
700 °C	Al_2O_3	25.9	64.5	0	9.6
	AlON	31.6	44.2	16.8	7.4
1000 °C	Al_2O_3	27.5	60.4	0	12.1
	AlON	31.7	45.7	13.5	9.1

The chemical compositions of the films annealed at 700 °C and 1000 °C have been examined by XPS. The results are given in Table 1. Obviously, nitrogen has been doped into Al_2O_3 thin films successfully for the films annealed in the wet ammonia. The nitrogen content in the AlON film grown at 1000 °C is slightly lower than that grown at 700 °C, implying nitrogen loss may occur at a higher anneal temperature. The ratios of N to O are about 1:2.6 and 1:3.4 for the AlON films grown at 700 °C and 1000 °C, respectively. Moreover, it should be noted that a small amount of silicon have been observed in both Al_2O_3 and AlON thin films, which should come from the silicon diffused to the surfaces of the films. The results also indicate that the higher the anneal temperature, the more severe the diffusion from the silicon substrates. The chemical bonding states of elements in the Al_2O_3 and AlON films have been analyzed by XPS as well. Figures 3(a)–3(d) show the XPS spectra of Al 2p, O 1s, N 1s, and Si 2p, respectively. For the undoped Al_2O_3 thin film, the peaks detected at 74.6 eV and 531.9 eV in Figs. 3(a) and 3(b) correspond to the Al 2p and O 1s peaks of Al–O bond in Al_2O_3, respectively. After nitrogen doping, both the position and the shape of Al 2p peak obviously change, as shown in Fig. 3(a). Two new peaks, occurring at 73.9 eV and 74.2 eV, can be assigned to Al–N and Al–O–N bonds, respectively. On the other hand, the nitrogen doping also causes a slight chemical shift of O 1s peak (see Fig. 3(b)) due to the formation of Al–O–N bond.

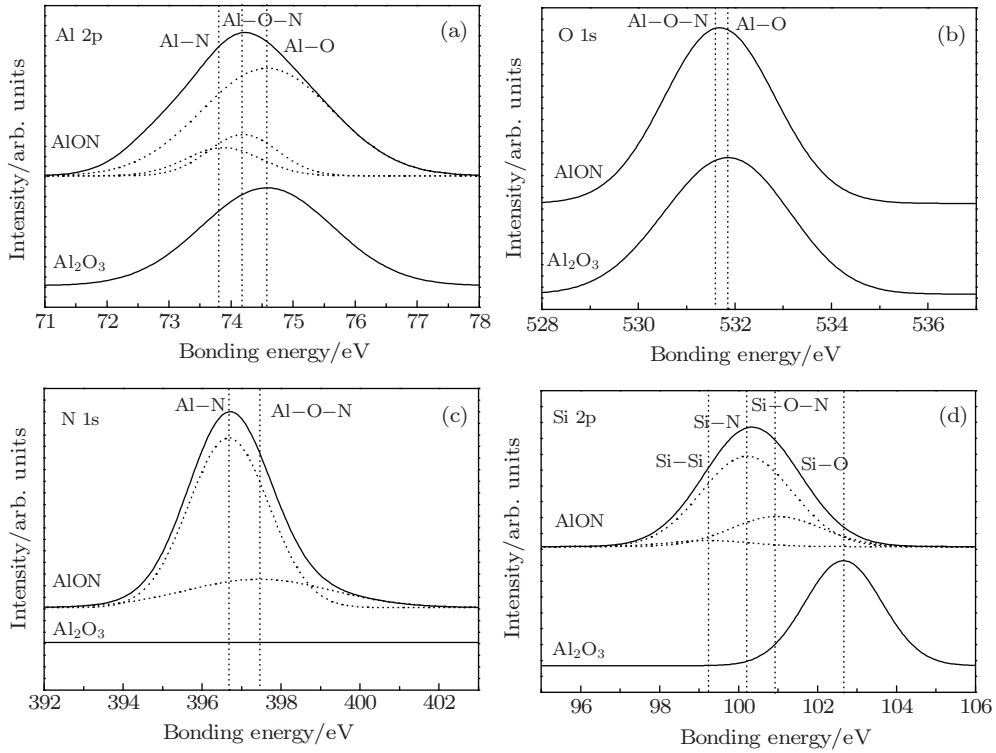


Fig. 3. XPS spectra of Al_2O_3 and AlON films: (a) Al 2p, (b) O 1s, (c) N 1s, and (d) Si 2p.

The bonding energies of Al 2p (74.6 eV) electron and O 1s (531.9 eV) electron, as shown in Figs. 3(a) and 3(b), prove that there are only Al–O bonds in the as-grown Al_2O_3 thin film. On the other hand, the shifts of the bonding energies of Al 2p (73.9 eV, Fig. 3(a)) electron and O 1s (531.6 eV, Fig. 3(b)) electron in the as-grown AlON thin film should come from the effect of nitrogen doping. These trends of shift are consistent with the literature results.[19] The N 1s spectra (Fig. 3(c)) indicates that the AlON films have been fabricated by the PAD technique successfully. The Al–N bond is evident since the bonding energy of N 1s electron is 396.8 eV. The broadening of the N 1s spectrum comes from the existing of Al–O–N bond (397.9 eV) in the AlON thin film. As shown in the Si 2p spectra (Fig. 2(d)), Si–N (100.3 eV) and Si–O–N (101.0 eV) bonds may come from the reaction between AlON thin film and Si substrate, and only Si–O bonds exist in the as-grown Al_2O_3 film. All the XPS data analyses are based on the NIST XPS database.

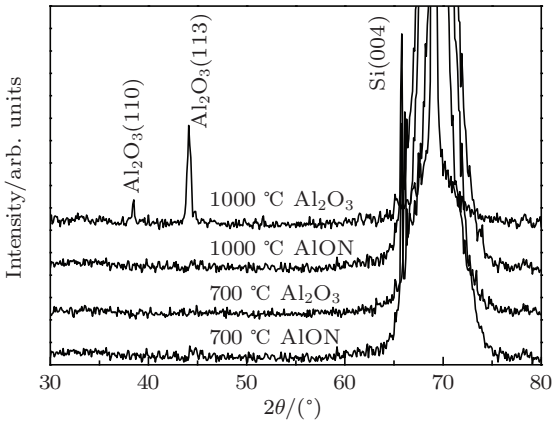


Fig. 4. XRD patterns of Al_2O_3 and AlON thin films deposited at different annealing temperatures.

XRD patterns from θ–2θ scans of Al_2O_3 and AlON thin films deposited at 700 °C and 1000 °C are shown in Fig. 4. No obvious peak is observed in the films annealed at 700 °C except the Si(004) diffraction peaks in the patterns of either Al_2O_3 or AlON thin films. This result indicates the amorphous or microcrystalline nature of both films, which may be attributed to the relatively low annealing temperature. When the annealing temperature is increased to 1000 °C, a polycrystalline Al_2O_3 thin film is formed as evidenced by the (110) and (113) diffraction peaks of the Al_2O_3 thin film. However, there are no obvious peaks in the pattern for the AlON thin film annealed in wet ammonia at 1000 °C, suggesting that the nitrogen doping may have suppressed the crystallization of the film. The phenomenon is similar to the previous observation in HfSiON thin films, which has proved that the nitrogen may suppress the crystallinity of oxide films.[11] This may be favorable for the applications of the films as the dielectric layers in MIS devices, as the amorphous layers would reduce the leakage currents through the grain boundaries.

Figure 5 shows the thermal conductivities of Al_2O_3 and AlON thin films measured from 80 K to 300 K. From Fig. 5, we can conclude that within this temperature region, the thermal conductivities of the as-grown AlON thin films are higher than those of the Al_2O_3 thin films annealed at the same temperature. The thermal conductivities of AlON thin films at 300 K are 0.62 W/m·K and 0.79 W/m·K for the films annealed at 700 °C and 1000 °C, respectively, while they are 0.37 W/m·K and 0.68 W/m·K for the Al_2O_3 thin films annealed at 700 °C and 1000 °C, respectively. It is known that AlN has higher thermal conductivity than Al_2O_3, which can be explained by that the Al–N bond shows stronger covalent bonding than the Al–O bond.[33,34] Similarly, the higher thermal conductivities of AlON thin films should be attributed to the stronger bond of Al–N bonding. On the other hand, it is also shown in Fig. 5 that the higher the annealing temperature is, the higher the thermal conductivity can be achieved for both the AlON and Al_2O_3 films. This result is reasonable since a better crystallinity should result in a higher thermal conductivity due to less phonon scattering by disordered areas in the lattice.[33] And a higher annealing temperature would improve the crystallinity for the films. The trends of thermal conductivity of the AlON and Al_2O_3 films indicate that the thermal performance of both kinds of thin films should be influenced by the crystallinity and the bonds in the films. Higher crystallinity and more Al–N bonds in Al_2O_3 thin films would enhance the thermal conductivity. However, as mentioned above, XRD results have demonstrated that the nitrogen doping in Al_2O_3 films would suppress the crystallization of the films. Thus, the effect on thermal conductivity from the nitrogen doping in the Al_2O_3 films is the competition between the stronger Al–N/Al–O–N bonding and a worse crystallinity. For the amorphous or microcrystalline films grown at 700 °C, the nitrogen doping enhances the thermal conductivity about 67% (from 0.37 W/m·K to 0.62 W/m·K) when measured at 300 K. However, at a higher annealing temperature, i.e., 1000 °C, the enhancement of thermal conductivity is only 16% (from 0.68 W/m·K to 0.79 W/m·K) when measured at 300 K, the lower enhancement may

be related to the much worse crystallinity of the as-grown AlON films compared to the Al_2O_3 films and the loss of nitrogen at this high annealing temperature. In practical applications, the processing temperatures have a certain limitation, which makes the nitrogen doping in a relatively low processing temperature a useful and effective way to improve the thermal conductivities of Al_2O_3 thin films.

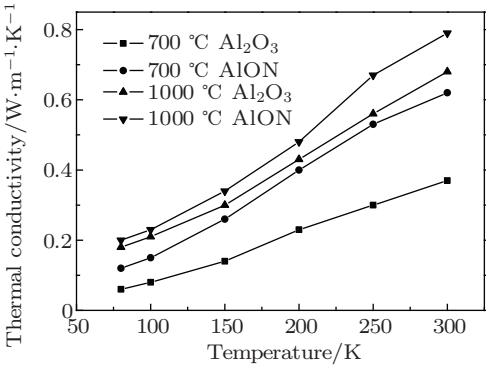


Fig. 5. Thermal conductivities of Al_2O_3 and AlON films at different temperatures.

4. Conclusion

Amorphous and polycrystalline Al_2O_3 and N-doped Al_2O_3 (AlON) thin films have been deposited on Si(100) substrates by using the PAD technique. The results of thermal conductivity showed that both nitrogen doping and annealing temperature have influences on the thermal conductivities of the thin films, which may be related to Al–N/Al–O–N bonding, crystallinity, and the contend of nitrogen in the films. On the other hand, it was also found that the nitrogen doping in the Al_2O_3 thin film would not only induce Al–N/Al–O–N bonding but also suppress the crystallization. The results demonstrated that at a relatively low processing temperature, the nitrogen doping is an effective way to improve the thermal performance of Al_2O_3 thin films. A 67% enhancement in thermal conductivity has been achieved for the samples grown at 700 °C.

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