Atomic layer deposition Al_2O_3 thin films in ECR plasma source

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Abstract: ALD Al_2O_3 thin films were accomplished by electron cyclotron resonance (ECR) plasma-enhanced chemical vapor deposition using trimethyl aluminum (TMA) and O_2 as precursor and oxidant, where argon was kept flowing in whole deposition process as a purge and discharge gas. The more than 3.2 Å/ purging cycle deposition rate and 8.3 dielectric constant of deposited Al_2O_3 was obtained even without extra heating, which were characterized including X-ray photoelectric spectroscopy (XPS), atomic force microscopy (AFM) and high resolution transmission electron microscopy (HRTEM). Deposition rates and surface morphology affected by RF bias potential were emphasized in in this paper.

Key words: ECR, atomic layer deposition, Al_2O_3

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Introduction

Atomic layer deposition (ALD) is a thin-film deposition technique in which the precursors, reactants, and purge gas are separately flowed into the chamber. Based on this special flowing controllable a good stoichiometry with perfect uniformity film can be fabricated. Due to the nature of the self-limited reaction by ALD, it is possible to achieve excellent step coverage and accurately control the film thickness besides the precise chemical stoichoimetry [1]. These merits indicate that the ALD method is the most suitable method for growing high-quality film used in sensors, catlaysises and high-k oxides.

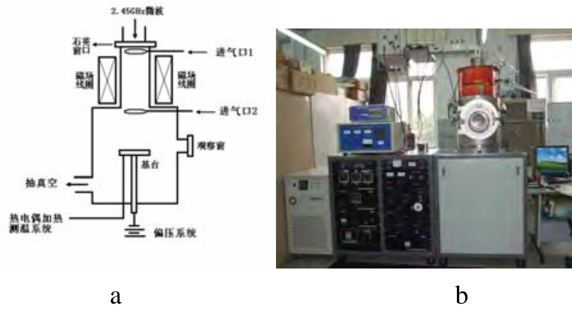
With regarding to the application in metal-oxidant semiconductor (MOS) ALD is an excellent deposition method for high-k film growth due to its superb process controllability, even for extremely low thickness high-k dielectrics [2-4]. In here Al_2O_3 [5] have been considered as promising oxide materials.

Recent ALD Al_2O_3 by chemical vapor deposition (CVD) is met severe challenge, such as the low deposition rate, the narrow temperature window, and limted precursor. To overcome these drawbacks and widen the ALD process window, plasma assisted CVD (PACVD) demonstrate an alternative approach for ALD fabrication. O_2 plasmas [6-8] and O_3 [9-11] have recently been considered as alternative oxidants. Particularly O_2 plasmas are very effective oxidants that can easily remove organic ligands by O-radical driven combustion-like surface reactions [12]. Therefore, the PACVD process generally yields more process flexibility [13], including the potential of depositing higher quality materials at lower substrate temperatures while also avoiding the use of the difficult-to-purge H_2O.

The PACVD processes utilized in recent includes the direct plasma ALD, where the substrates are positioned on an electrode used for plasma generation [14, 15], remote plasma ALD, where plasma generated remotely from the substrate but with all plasma species still present at the position of the substrate [16, 17] and radical enhanced PA-ALD, where the plasma is generate far from the substrate such that ions and electrons from the plasma do not reach the substrate at all [18]. For direct PA-ALD it was considered that plasma damage can occur due to high ion energies [19, 20] and not suitable for the film deposition due t the etching.

In this paper, we also deposited nano-Al_2O_3 by PA-ALD. Defferent from the recent PA-ALD route, the electron cyclotron resonance PA-ALD (ECR-PA-ALD) with a biased radio frequency (RF) on substrate was employed. In experiments trimethylaluminum (TMA, Al $(CH_3)_3$) (as the aluminum precursor) and O_2 plasma (as an oxygen source) were still utilized as previous. X-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM) and high resolution transmission electron microscopy (HRTEM) were used to characterize the Al_2O_3 films. The morophology of Al_2O_3 affected by RF bias were investigated in detail.

Experiment



a b

Fig.1 a-the schematic digram of ECR-PA-ALD fro Al2O3; b-the photo of plasma setup

Al_2O_3 films were deposited on p-Si (100) substrates by using ECR-PA-ALD with $Al(CH_3)_3$ (99.99%) as the aluminum precursors and O_2 (99.999%) plasma as an oxide source. The temperatures of Al_2O_3 growth was maintained at ambient temperature, varying from 25~40^{0}C during the whole process. The Al source was carried by Ar gas at 20sccm. The ECR plasma power was changed from 250~550 W and biased RF was varied from 0 to 150W. Before mounted to the substrate, the p-Si substrates were dipped in a diluted HF ($HF:H_2O$=1:100) solution and then rinsed in de-ionized water. The injection times of the Al source, and O_2 plasma were vared from 5 s to 20s, respectively.

The morophology of the films were characherized by atomic force microscopy (AFM, CSPM3000, BenYuan China), and x-ray photo electron spectroscopy (XPS, Kratos Axis ULTRA, using a monochromatic Al *Kα* source and a charge neutralizer). The interface between Al_2O_3 and substrate p-Si (100) were scanned by transmission electron microscopy (TEM, JEOL 2010F, 200 kV field emission gun).

Results and discussion

Basic pressuer of ECR was 5×10^{-4}Pa, and the working pressure was 0.01~0.5Pa. The parameters for ALD Al_2O_3 are listed in Table 1.

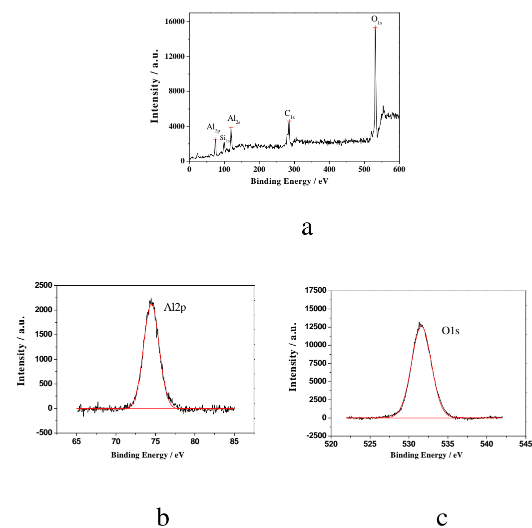
Table 1 the Al2O3 ALD precessing parameters in ECR plasma

Power (W)	250~550
Ar purge time and rate (s/sccm)	5~20/20~40
O_2purge time and the rate (s/sccm)	6~20/10~20
Carrier gas Ar(throght TMA bubble) purge time and rate(s/sccm)	1~12/20~40
Biased RF (W)	0~150
Substrat temperature(^{0}C)	ambient~40
Numver of cycle	20~400

XPS measurements were carried out after 100 cycles ALD Al_2O_3 smaple. The analysis was performed using an aluminum source, pass energy of 187.85 eV and an energy step of 0.8 eV. In Fig. 2 (a), the spectrum shows a weak C 1s peak at 284.7 eV, strong O1s peak at 531.9eV and weak at Al2s peak at 119.0 eV, Al2p peak at 74.3 eV.

The XPS results verify the composition of the deposited Al_2O_3 films on the p-Si (100) substrate. In Fig 2(b) after fitted the XPS spectra of Al2p peak consist of only single peaks centered around 74.9 eV, which corresponds to Al–O bonds of Al_2O_3 [21]. The Al 2p spectra of the as deposited samples could not be deconvoluted into more than other peak. It indicates that the film consists mainly of homogenous Al_2O_3 without Al–Al clusters or substoichiometric alumina in the film [22, 23].

It is clearly evident from the XPS spectra of O1s peak shown in Fig. 2(c), that the O1s core also consistes of only single peaks centered around 531.9 eV, which corresponds to Al-O bonds of Al_2O_3. The Al to oxygen ratios (Al/O) of film calculated by the ratio of the peak area Al to O peak area ratios is 1.93/3, near to stoichoiometry ratio of Al_2O_3. These results imply that the films grown on the bare Si wafers contain the concentration of excess oxygen. The Si2p core loss spectrum was also appeared from the Si substrate at peak of 98.6 eV, it corresponds to bulk Si since there are no other peaks in spectrum [24].



a

b c

Fig. 2. X-ray photoelectron spectroscopy spectra of (a) alumina after 100 cycles; (b) Al2p; (c) O1s

The high-resolution transmission electron microscope (HRTEM) Figure 3 shows the cross-sectional HRTEM

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image of a p-Si/SiO_2/Al_2O_3 structure. The thicknesses of the SiO_2, and Al_2O_3 were found to be 0.5nm and 80nm, respectively. The HRTEM image reveals that the Al_2O_3 film is ~80 nm, indicating that the growth rate of Al_2O_3 at ambient temperature was 0.32 nm per cycle. It is much higher than that deposted in similar condition samples [25, 26]

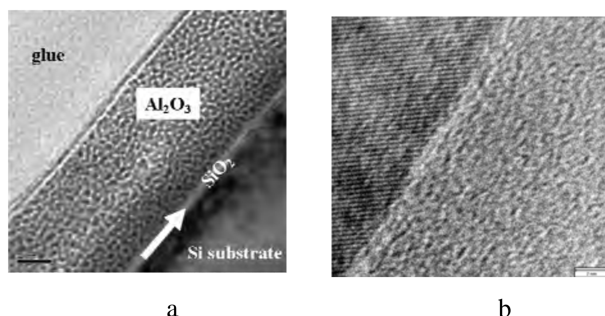

Fig. 3 cross-section HRTEM of Al_2O_3 (The scale bars are.a-20nm; b-2nm)

The influence of the bias voltage on the ALD Al_2O_3 was examined by AFM images. The growth conditions were listed in Table 2. The surface morphology of Al_2O_3 on p-Si substrates was investigated on area of 5 μm * 5μm. The results were compared as shown in Fig. 4 and Table 2. The root-mean-square (RMS) surface roughness of the ~80 nm-thick Al_2O_3 film on p-Si substrate was estimated to be 4.4 A when no bias RF was applied. However, with the bias RF, not only at low 50W, but at high 150W, the RMS was always reduced. It seems the RMS decreased along with the bias RF power. The reason of bias RF improving the RMS and the increasing deposition rate, is still under study. But the role from ionic radicals is certainly important.

The dielectric constant k was measured which is 8.3 in the p-Si substrate for 250 cycle, 80nm Al_2O_3, it means the dielectric insulator Al_2O_3 has a high-quality, almost twice that of SiO_2.

Table 2 the deposition parameters ang the bias voltage (250 cycle)

No	Ar purge timeand flow rate	TMA purge time and flow rate	O_2 purge time and flow rate	RF bias Power (W)	ECR power (W)	Substrate temperature (^{0}C)	RMS(nm)
1	20S/30sccm	4s/20sccm	10S/15sccm	no	300	Ambient (~40^{0}C)	0.44
2	20S/30sccm		10S/15sccm	50			0.37
3	20S/30sccm		10S/15sccm	100			0.35
4	20S/30sccm		10S/15sccm	150			0.32

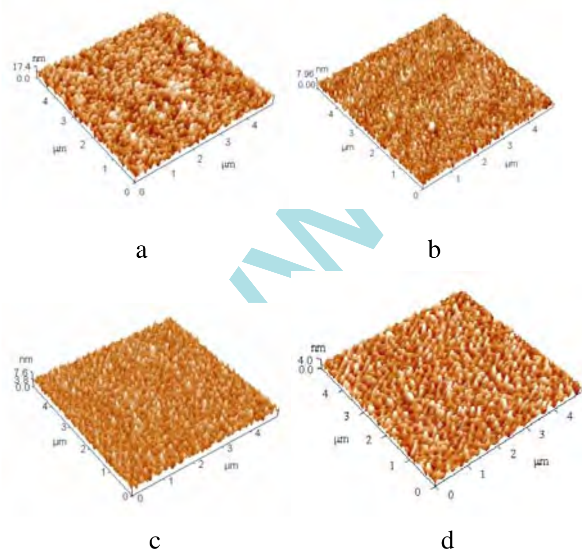

Fig. 4 AFM images of 80 nm-thick Al_2O_3 film grown by ALD on p-Si substrates relation to the RF bias. a-0W, b-50W,c-100W, d-150W

Conclusion

With the ECR plasma enhanced ALD, dielectric Al_2O_3 layer was doposited on p-Si substrate. In here the RF bias for the ALD Al_2O_3 was emphasized. It is obtained the RF bias not only increased the growth rate of ALD, but improved the film surface mofphology, the higher RF bias power the smaller RMS. The possible reason is explained from the charged radicals, which affected significantly by the bias voltage.

Acknowledgements

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