

Interfacial Structure of Ta₂O₅/Si Film and Photoactivity

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Abstract: Tantalum oxide (Ta₂O₅) thin film photocatalysts were prepared on single crystal Si(110) substrates *via* sol-gel and spin coating methods. Ta₂O₅ crystallinity was improved, and the crystal size became larger with the increase of heat-treating temperature. The interface diffusion and reaction of the film were studied by using Auger electron spectroscopy (AES) depth profile and line shape analysis. Diffusion was dominant at the interface layer when the calcination temperature was below 700 °C. When the temperature reached 800 °C, both interface diffusion and reaction occurred. The photocatalytic activity was studied using aqueous salicylic acid as a degradation probe molecule under UV-light irradiation. It was found that Ta₂O₅/Si film showed a photocatalytic activity similar to that of TiO₂/Si film.

Key Words: Ta₂O₅/Si thin film; Auger electron spectroscopy; Interface diffusion; Interface reaction; Photocatalytic activity

Recently, tantalum oxide (Ta₂O₅) has attracted extensive interest because of its potential application in many regions. It shows high dielectric constant (30–35), chemical and thermal stability^[1], and is easily compatible with silicon technology^[2]. Because of its high reflective index, low absorptivity, and broad range of transmittance spectrum (300 nm–10 μm), Ta₂O₅ has wide application in the field of optical engineering. It can also be used as a protective film because of its high rigidity^[3]. Besides, Ta₂O₅^[4] and many other tantalates were found to show photocatalytic activity, such as KTaO₃^[5], In-TaO₄^[5–8], and NaTaO₃^[9]. The studies that have involved Ta₂O₅ have mainly focused on the photocatalytic performance of Ta₂O₅ powders^[4]. However, few of the studies have focused on photocatalytic activity of its film.

Ta₂O₅ has been prepared through several processes: electron beam evaporation, direct current reactive magnetron sputtering, ion-beam assisted deposition (IAD), chemical vapor deposition (CVD), ion-beam sputtering, and so on^[2]. However, these methods still have certain disadvantages, for instance, film with crystal structure cannot be prepared by electron beam evaporation, and the repetition is poor; the adhesive force of the film prepared through this process is limited. It is difficult to control the stoichiometry ratio of films through ion

beam reactive sputtering and IAD routes. CVD method is always unsafe because of the requirement of high temperature and large amount of hydrogen. In addition, the sol-gel method is a kind of potential film preparation process, which possesses advantages of chemical homogeneity, convenient adjustment of components, possibility of obtaining homogeneous multi-component film, and low annealing temperature and cost^[10].

In this article, Ta₂O₅/Si film was synthesized *via* sol-gel method. The interface diffusion and reaction of the film were studied by using Auger electron spectroscopy (AES) depth profile and line shape analysis. Its photocatalytic activity was also studied by using degrading aqueous salicylic acid under UV-light irradiation.

1 Experimental section

1.1 Preparation of precursor solutions

Commercially available TaCl₅ (A.R., butanol as solvent) were dropped into C₂H₅OH (A.R.). Diethanolamine (A.R.) (1%(w)) was added as stabilizer. The precursor solution was obtained after stirring for 4 h at room temperature.

TiO₂ sol was prepared by adding commercial Ti(OC₄H₉)₄ (A.R.) into C₂H₅OH (A.R.) to form a 10%(w) solution.

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1.2 Preparation of Ta₂O₅/Si and TiO₂/Si thin films

Single crystal Si(110) substrates with an area of 1 cm×1 cm were dipped in diluted HCl solution, and then they were rinsed by distilled water. The films were formed on clean Si substrates by spin coating (KW-4 Spin Coater) different precursor solutions with a spin velocity of 500 r·min⁻¹ for 9 s and then 3000 r·min⁻¹ for 30 s. The film was exposed to air for 3 min. The steps of dipping the solution and spin coating were then repeated to obtain films with different layers. After drying at 80 °C for 2 h, the films were annealed at a temperature range from 500 to 800 °C for the definite time in an air-flow oven.

1.3 Characterization

The crystal structure of the films was investigated by using X-ray diffraction (XRD) (Rigaku D/MAX-RB diffractometer) with Cu K_α radiation and a scan rate of 4 (°)·min⁻¹. AES spectra were obtained by using a PHI 610 scanning AES system. The beam voltage was 3.0 kV and the beam current was 0.5 μA. The energy and beam current of Ar ion beam were 3.0 keV and 4.5 μA, respectively. The diameter of the beam was 1 mm. The electron beam was incident at an angle of 60° with respect to the specimen surface to make the sample surface perpendicular to the ion beam. The sputtering rate was approximately 30 nm·min⁻¹ for a thermally oxidized SiO₂ thin film. The operation process in the ultrahigh vacuum system was controlled to 2×10⁻⁷ Pa.

A UV-light lamp of 11 W (λ = 254 nm) was used to degrade aqueous salicylic acid (SA, c₀=6×10⁻⁵ g·L⁻¹). The film was fixed in a small container with 5 mL SA solution in each experiment. The distance between UV lamp and film was 5 cm. The average light intensity was 108 μW·cm⁻². After irradiation, the solution was analyzed by using Hitachi U-3010 UV-Vis spectrophotometer.

2 Results and discussion

2.1 Crystallinity of Ta₂O₅/Si film

From the XRD patterns^[12] of Ta₂O₅/Si film annealed at different temperatures, it was found that β-Ta₂O₅ with orthorhombic phase formed at 500 °C. The film was polycrystalline and (1 $\bar{1}$ 0) partial orientation preferred. With the increasing of annealing temperature, the intensity of diffraction peaks gradually increased. The number of the peaks increased at 700 °C, suggesting that the crystal became more perfect. The crystal size of Ta₂O₅ film was measured by using Sherrer formula^[13]. Its crystal diameters were increased from 20.4 nm, 23.4 nm, and 26.0 nm to 34.8 nm when the annealing temperatures were 500 °C, 600 °C, 700 °C, and 800 °C, respectively.

2.2 Interface diffusion and reaction of Ta₂O₅/Si film

2.2.1 Chemical state of the surface

Fig.1 shows the AES surface spectrum at the surface of the Ta₂O₅/Si film annealed at 600 °C. The AES kinetic energies of Ta MNN are 154, 166, and 176 eV, which are in accordance with literature^[14]. Therefore, typical Ta–O bond formed on the surface of the film. C KLL peak at the surface layer with the AES kinetic energy of 272 eV attributed to the carbon surface contaminations. This signal disappeared after surface sputtering. Typical O KLL peak was shown at 512 eV, which was also in agreement with literature^[14]. No peaks appeared at 92 eV (Si LVV), indicating that the substrate Si had been completely covered by Ta₂O₅.

2.2.2 The influence of annealing temperature on the interface layer of Ta₂O₅/Si film

The AES depth profiles of Ta₂O₅/Si film with 3 layers annealed at 500, 600, 700, and 800 °C were shown in Fig.2. Because the sputtering rate was high and the results were obtained by comparing with the standard data, preferential sputtering and element segregation can be neglected. In general, the portion of the film layer where the atomic concentration of Si is between 20% and 80% can be considered as the interface layer. The distance from surface to the layer where the atomic concentration of Si is 20% is known as the thickness of Ta₂O₅ film layer. It was found that the thicknesses of films prepared at different temperatures were almost same when the concentrations of the precursors were same. The thicknesses of the films annealed at 500, 600, and 700 °C were between 51 and 55 nm. However, the film annealed at 800 °C was thinner (approximately 45 nm). This may be caused by the serious diffusion of Si substrate at this temperature.

The ratio of O to Ta remained stable with the increasing of the film depth, indicating the uniform composition of the film. The concentration of Ta at surface was lower than in the interior, whereas the concentration of O at the surface, which was composed of Ta–O (61.3%) and surface O–H (48.7%) was higher than that in the interior. The interface layer between film and Si substrate was wide, indicating the occurrence of interface diffusion during annealing. Therefore, the diffusion of Si cannot be prevented by the formation of Ta₂O₅ crystal.

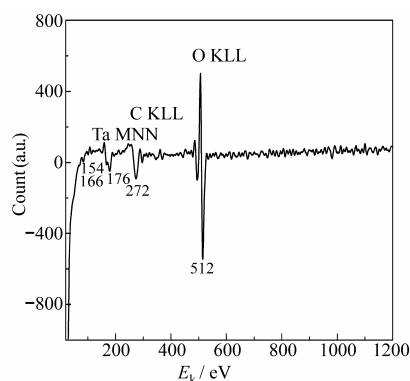


Fig.1 AES surface spectrum of the Ta₂O₅/Si film

When the annealing temperature was below 800 °C, Ta and O in the interface layer decreased with the increasing of film depth, whereas Si increased with the depth. Interface diffusion, not interface reaction, was dominant at the interface layer at these temperatures. The thicknesses of Ta₂O₅/Si film annealed at 500, 600, 700, and 800 °C for 4 h were 31.0, 31.3, 33.0, and 43.0 nm, respectively. The thickness increased with the annealing temperature. The diffusion was interdiffusion of three elements, not self-diffusion of one element. This was because that the concentration of Ta, O, and Si in the interface layer gradually changed with the sputtering. A 15 nm flat layer of SiO₂ appears when the film was annealed at 800 °C. The chemical states of Si were analyzed by linear least squares fitting, implying that both SiO₂ and Si existed in the film. The ratio of O to Si of SiO₂ species was 2 at this depth, suggesting that Si and O diffused intensely and reacted to form SiO₂ at this temperature. The Ta₂O₅ crystal grown at this temperature was not compact enough to depress the diffusion of Si. However, the diffusion of Ta was suppressed greatly by the SiO₂ layer. The concentration of Ta was very low when sputtering for 2 min.

2.2.3 AES line shape analysis of Ta₂O₅/Si film annealed at 700 and 800 °C

The AES line shapes of Ta MNN, O KLL, and Si LVV from the films annealed at 700 and 800 °C are shown in Fig.3. No

charging phenomenon was observed during the sputtering because the film was thin and the substrate used in this study was low-resistive semiconductor Si. The AES kinetic energies of the elements from surface to Si substrate did not change, suggesting that the Ta₂O₅ had formed stably on the substrate. As the diffusion abilities of elements and the distribution of elements were different, their chemical states were not same at various depths.

Ta MNN has three peaks. The highest AES kinetic energy of Ta MNN for pure Ta and Ta₂O₅ are 179 and 176 eV, respectively^[15] (All the Ta MNN peak mentioned below referred to this peak). The energies of Ta in Fig.3a from the surface to Si substrate are lower than that of pure Ta, indicating the loss of electrons and oxidation of Ta. The AES kinetic energy of Ta did not decrease with the depth homogeneously. Ta₂O₅ was dominant Ta species from depth A to C. O decreased with the film depth from layer C to depth D; therefore, the oxidation degree of Ta must be diminished. However, the diffusion of O in the interface layer was faster than that of Ta, so O/Ta was higher than in the depth C, which enhanced oxidation degree of Ta and decreased AES kinetic energy. Ta could not be detected in depths E and F where the substrate was present. Compared with the AES line shape of Ta MNN from the film annealed at 800 °C in Fig.3b, the AES kinetic energy of Ta MNN from film annealed at 700 °C was higher, implying the deeper oxidation degree of Ta at higher temperature. The sig-

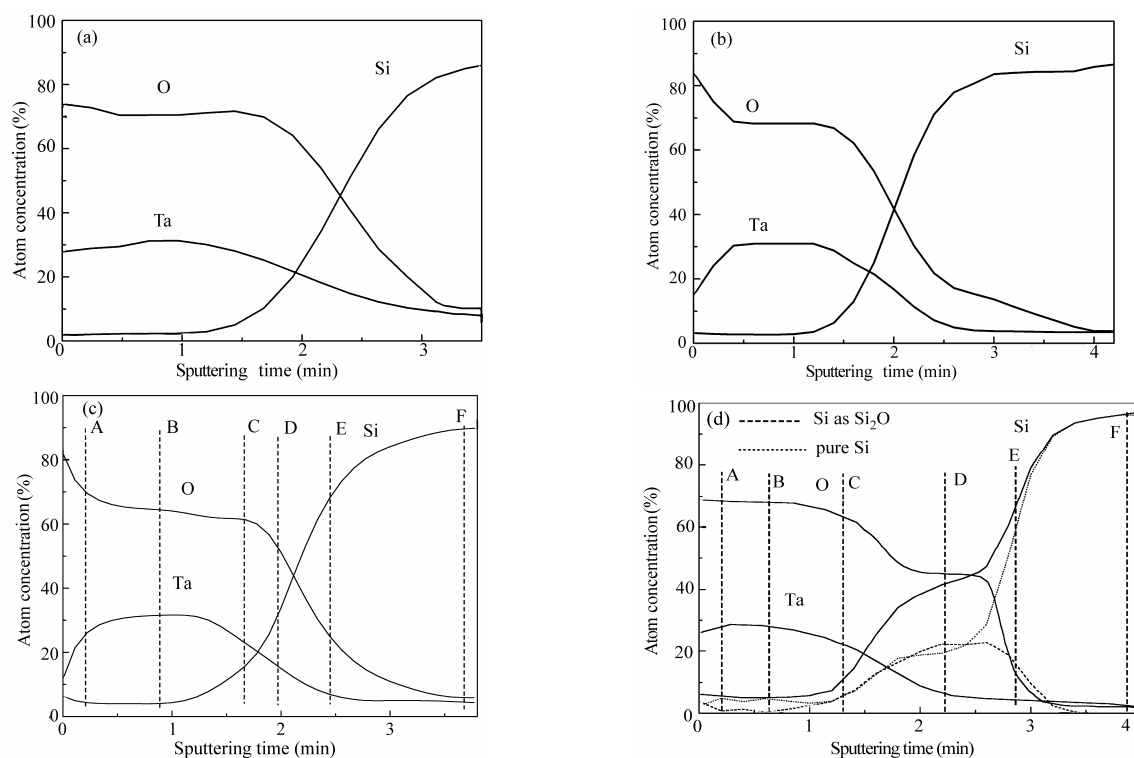


Fig.2 AES depth profile spectra of the three layers of Ta₂O₅/Si (110) film samples annealed at different temperatures for 4 h a) 500 °C; b) 600 °C; c) 700 °C; d) 800 °C. The film was prepared using 10% ethanol precursor solution. A, B, C, D, E in 2c and 2d are used to identify different depths in the film.

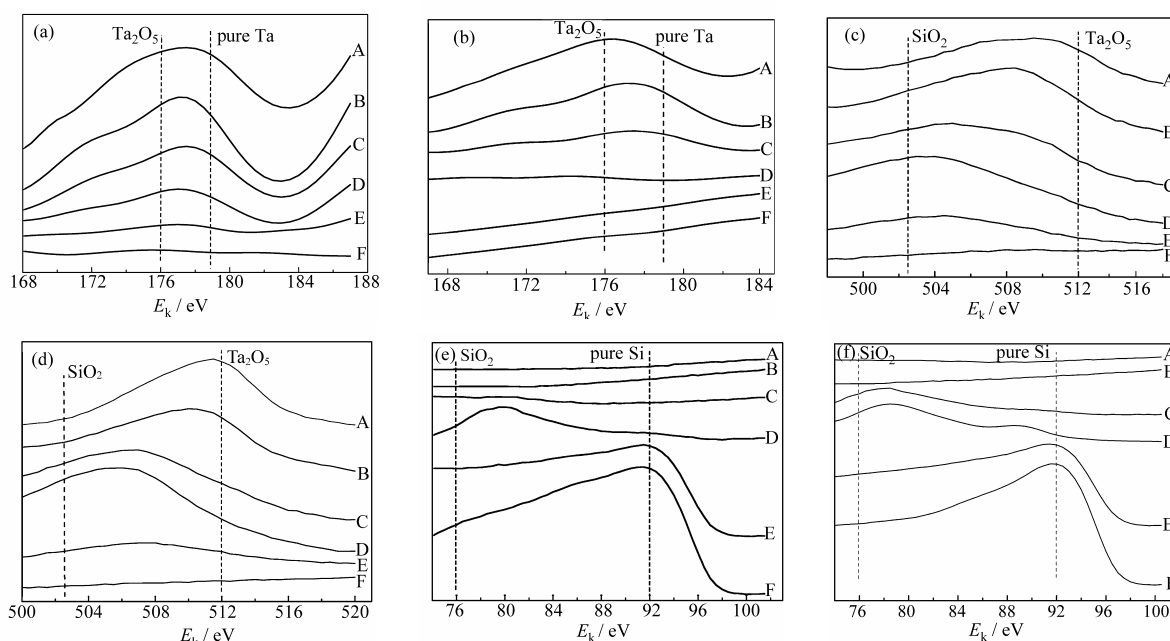


Fig.3 AES line shape analysis of three layers of $\text{Ta}_2\text{O}_5/\text{Si}$ films annealed at 700 and 800 °C

a) Ta MNN (700 °C); b) Ta MNN (800 °C); c) O KLL (700 °C); d) O KLL (800 °C); e) Si LVV (700 °C); f) Si LVV (800 °C)

Lines A–F are used to identify the AES line shapes at different depths from the layer after 0.2 min sputtering to Si substrate, which correspond to the depths of A–F in Fig.2c and Fig.2d.

nal of Ta was weak at depth D, as the SiO_2 layer stopped the diffusion of Ta.

The AES line shape of O KLL is shown in Fig.3c and Fig.3d. The kinetic energy of O decreased with the increasing film depth. This was because the diffusion of O was faster than Ta. O/Ta increased with the sputtering when there was no occurrence of oxidation of Si. The electron, that O received, reduced until O signal disappeared at depth E. The peaks of O KLL in $\text{Ta}_2\text{O}_5/\text{Si}$ film prepared at 800 °C for 4 h was more complicated. The AES peak shifted to low energy from surface to depth B, which attributed to the electron loss of O. The peak changed at depth C that resulted from the existence of SiO_2 and Ta_2O_5 . O can gain electron from Ta more easily than from Si, so the kinetic energy of O from Ta_2O_5 was higher than that from SiO_2 . Ta_2O_5 took the main part at the depth C, but the peak shift to low energy at depth D resulted from the enrichment of SiO_2 .

Si near the interface layer was slightly oxidized when the film was annealed at 700 °C. The peak of Si shifted to the pure Si energy with the sputtering. An AES peak of Si appeared at 76 eV near the energy of SiO_2 at depth D, indicating the weak oxidation of Si. When sputtering to Si substrate at depth D, the peak corresponded to the peak of pure Si. A peak of Si appeared at 76 eV referred to SiO_2 at depth C and D. This was because the diffusion of Si was more intense and reacted with O to form a SiO_2 layer when the film was annealed at 800 °C. A peak at 92 eV is also shown at depth D (Fig.3f) implying the coexistence of pure Si with SiO_2 .

2.3 Photocatalytic performances of $\text{Ta}_2\text{O}_5/\text{Si}$ film

Ta_2O_5 is a semiconductor with band gap of 3.0 eV. The conduction band is from Ta 5d, and the valence band is composed of O $2p^{15}$. The photocatalytic activity of the as-prepared $\text{Ta}_2\text{O}_5/\text{Si}$ thin film was measured by the degradation of aqueous salicylic acid under UV irradiation in Fig.4. As the thickness of the film was only 51 nm and the area was about 1 cm \times 1 cm, the amount of the catalyst on the film was very small. As a result, the decomposition process was slow. The photocatalytic activity of $\text{Ta}_2\text{O}_5/\text{Si}$ film annealed at 600 °C for 4 h was

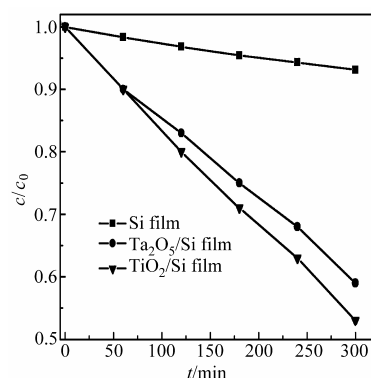


Fig.4 Photocatalytic degradation of salicylic acid (SA) over $\text{Ta}_2\text{O}_5/\text{Si}$ and TiO_2/Si films under UV-light irradiation

$\text{Ta}_2\text{O}_5/\text{Si}$ film is prepared at 600 °C for 4 h, and the TiO_2/Si film is prepared at 450 °C for 1 h. Both the films consist of three layers.

c_0 : the initial concentration of the SA solution; c : the concentration of SA solution at different times

compared with that of TiO₂/Si film, which is well known as a high activity photocatalyst. It can be observed that 50% salicylic acid was degraded by Ta₂O₅/Si film and TiO₂/Si film in 5 h, but no salicylic acid was decomposed by Si film without catalyst. From this result, it was found that Ta₂O₅/Si film and TiO₂/Si film had similar photocatalytic activity. The Ta₂O₅/Si film prepared by sol-gel and spin coating methods presented good photocatalytic activity.

3 Conclusions

Ta₂O₅ thin films with orthorhombic structure were synthesized through sol-gel and spin coating methods. Ta₂O₅ crystal was formed at 500 °C and it became more perfect with the enhancing of annealing temperature. Interface diffusion was dominant when the annealing temperature was between 500 and 700 °C, but interface reaction was the governing step when the annealing was 800 °C. The diffusion of Ta, O, and Si from films annealed at various temperatures and the AES line shapes of the elements at various depths were different because of their different chemical characteristics. All these can influence the physical and chemical properties of the film. Ta₂O₅/Si film annealed at 600 °C for 4 h had similar photocatalytic activity with that of TiO₂/Si film by degradation of salicylic acid solution under UV-light irradiation, indicating the good photocatalytic activity of the Ta₂O₅/Si film.

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