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Study on Fabrication of Yttrium Oxide Thin Films Using Mist CVD

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Abstract

Yttrium oxide thin films were fabricated by Mist CVD with two solution chambers. In order to obtain the films at low temperature, H_2O and NH_3 (aq) were selected as assistant materials to support the fabrication process. The effect of H_2O and NH_3 (aq) on the deposition rate and refractive index of the yttrium oxide thin films were studied. The experiment results reveal that H_2O and NH_3 (aq) have a positive effect on preparation of the high quality yttrium oxide thin films. However, the mechanism of H_2O and NH_3 (aq) effect on fabricating high quality yttrium oxide thin films needs further analysis.

1. Introduction

Yttrium oxide thin films have been considered as a potential material for oxide dielectrics because of its excellent electronic properties, such as high dielectric constant (14~18), large band gap (~5.5eV), high melting point (~2439°C), low absorption (from near-UV to IR region) and a relatively high refractive index (1.7 ~ 1.8) [1, 2]. In addition, yttrium oxide is also a constituent of several more complex materials. For example, yttrium iron garnet ($Y_3Fe_5O_{12}$, YIG) is composed of yttrium oxide and iron oxide. Therefore, the study on fabrication of high quality yttrium oxide thin films is propitious to fabricate the high quality YIG thin films. Yttrium oxide thin films are not only prepared by non-equilibrium reaction systems, such as electron-beam evaporation and pulsed-laser deposition [3, 4], but also can be prepared by equilibrium reaction systems, such as metal-organic chemical vapor deposition and atomic layer deposition [5, 6]. For equilibrium reaction systems, the deposition temperature should be set over 700 °C to obtain high quality yttrium oxide films. However, in this study, we planned to fabricate high quality yttrium oxide films at low temperature (below 400 °C) using mist CVD.

Previously, it was reported that supporting solution affected the reaction paths during thin film formation [7]. Thus, instead of using high deposition temperature, assistant solutions were selected to support the fabrication of high quality yttrium oxide. On the other hand, in mist CVD, the controlling of the atmosphere in reaction area has positive effect on fabrication of high quality thin films. Therefore, two solution chambers were used in mist CVD to control the atmosphere. The details of this homemade fine-channel type mist CVD system (FCM-CVD) have been reported in [8].

2. Experimental

In our work, yttrium oxide thin films were fabricated at 400°C. Different from the reported mist CVD system, two solution chambers (precursor solution chamber and assistant solution chamber) and one mixing chamber were used here. Tris (acetylacetonato) yttrium (III) ($Y(C_5H_7O_2)_3{\cdot}nH_2O$) ($n$=2.36 as determined by TG-DTA,) was selected as the precursor and dissolved in MeOH, the concentration was 0.01mol/L. Meanwhile, H_2O and NH_3 (aq) were chosen as the supporting materials, and MeOH was chosen as the solvent in the assistant solution. In this experiment, the precursor solution and assistant solution were contained in different solution chambers, N_2 was chosen as the carrier gas and dilution gas. The mist was generated separately and transferred by carrier gas to the mixing chamber, then the mixing mist is deposited in the growth unit. Silicon was selected as the substrate, which were cleaned by HF for 10 min. Post annealing was carried out in N_2 atmosphere, at 800 °C for 5 min.

Thermal analysis of $Y(C_5H_7O_2)_3{\cdot}nH_2O$ was carried out by TG-DTA (Hitachi STA7200RV), the heating rate was 5.0 °C/min and the gas rate was 50 ml/min (air). The spectroscopic ellipsometer (J.A. Woollam Japan WVASE) was employed to estimate the film thickness and refractive index, using the Cauchy model. The chemical bands were measured by Fourier Transform Infrared Spectroscopy (FT-IR). The characteristics of the films' surface morphology were obtained by Atomic Force Microscope (AFM).

3. Results and discussions

Figure 1 shows the thermal analysis result of $Y(C_5H_7O_2)_3{\cdot}nH_2O$. From Fig. 1, it can be seen that $Y(C_5H_7O_2)_3{\cdot}nH_2O$ was only partially decomposed to form yttrium product at around 380 °C, and decomposed to form $Y(OH)_3$ at around 550 °C, then decomposed to form Y_2O_3 at the temperature around 750 °C. The TG-DTA result suggests that yttrium oxide thin films will be obtained when the deposition temperature is over 750 °C.

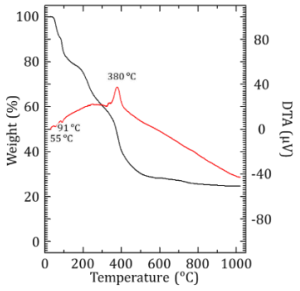

Fig.1 TG-DTA plots of $Y(C_5H_7O_2)_3{\cdot}nH_2O$

In order to fabricate yttrium oxide thin films at low temperature, several assistant solutions were selected to support the fabrication process. Figure 2 shows the effect of H_2O ratio (0%, 5%, 10%, 50% and 100%) and $[NH_3]/[Y]$ ratio (0.1, 0.2, 0.4 and 1.0) on the deposition rate and refractive index of the thin films, respectively. As seen in Fig.2 (a), with the increasing H_2O ratio in the assistant solution, the deposition rate of the thin films increased abruptly at 5% and then decreased gradually. In contrast, the films' refractive index increased from 1.6 to 1.7 as the H_2O ratio increased from 0% to 100%. In Fig.2 (b), when NH_3 was added to the assistant solution, the deposition rates were all lower than 5 nm/min, but the refractive indexes were over 1.75. From the results, it can be deduced that H_2O has positive effect on the deposition rate in the certain range, but with the increasing deposition rate, the refractive index decreased. Different with H_2O, NH_3 has positive effect on the increasing in refractive index but has negative effect on the increasing in deposition rate.

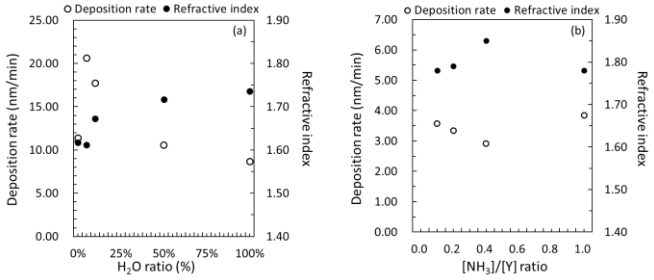

Fig.2 The deposition rate and refractive index of yttrium oxide thin films with (a) different H_2O ratio and (b) different $[NH_3]/[Y]$ ratio

For fabricating high quality yttrium oxide thin films, the assistant solution composed of MeOH (90%), H_2O (10%) and NH_3 (aq) (0.01 mol/L) was used, the thickness and refractive index of films were shown in Table I. Using this mixing assistant solution, the thin film with the thickness of 197 nm (deposition rate was 19.7 nm/min) and refractive index of 1.66 was prepared. However, these properties were almost same with the films fabricated by 90% MeOH and 10% H_2O as assistant solution (deposition rate was 17.7 nm/min and refractive index was 1.67). To improve the quality of the thin films, post annealing was carried out. After annealing, the film thickness decreased and the refractive index increased. It is considered that the carbon-related residuals remained in the film before annealing.

Table I Thickness and refractive index of thin films

Samples	Thickness, nm	Refractive index
Before annealing	197.05	1.66
After annealing	129.79	1.76

FT-IR results are shown in Fig.3. From the figure it can be seen that after annealing the ν (OH) group disappeared, and the intensity of ν (Y-C) and ν (Y-N) groups decreased, this may be one of the reasons for the decrease in film thickness after annealing. In addition, around 500 cm^{-1}, the band, corresponding to the Y-O bonding, is more intense in the film after annealing.

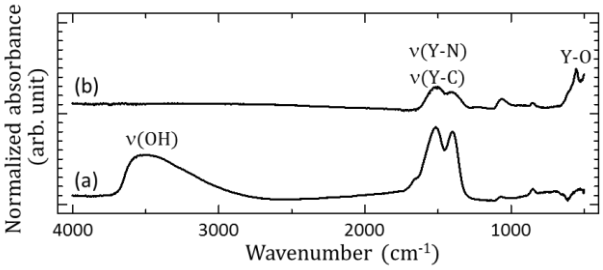

Fig.3 FT-IR patterns of yttrium oxide thin films (a) before and (b) after annealing

Surface morphology of the films is shown in Fig.4. In Comparison with before annealing, some holes formed on films surface after annealing. The RMS roughness of yttrium oxide thin films before and after annealing were all small, indicating that the samples have smooth surface.

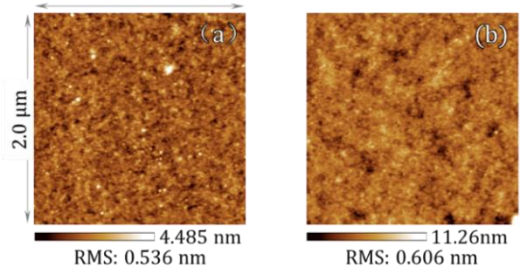

Fig.4 Surface morphology of yttrium oxide thin films: (a) before annealing and (b) after annealing

4. Conclusions

Yttrium oxide thin films were fabricated by mist CVD in this research. In order to control the atmosphere in the reaction area, two solution chambers were used in the mist CVD. For fabrication of thin films at low temperature, H_2O and NH_3 (aq) were selected as assistant materials, and the effects on deposition rate and refractive index of the thin films were studied. The experiment results show that H_2O and NH_3 (aq) have the positive effect on preparation of high quality yttrium oxide thin films, but the mechanism was not clear. In this experiment, post annealing was necessary to improve the properties of the yttrium oxide thin films.

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