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Effect of laser power on orientation and microstructure of TiO_2 films prepared by laser chemical vapor deposition method

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ABSTRACT

The TiO_2 films were prepared on Pt/Ti/SiO_2/Si substrate by a laser chemical vapor deposition method. With increasing laser power (P_L) from 48 to 98 W, the deposition temperature (T_{dep}) monotonously increased from 849 to 929 K. At T_{dep}=849 K (P_L=48 W), the rutile TiO_2 film was prepared with strong (110) and (200) peaks. With increasing T_{dep} from 849 to 883 K (P_L=71 W), the intensity of (110) peak increased. The (110)-oriented TiO_2 films were obtained for T_{dep} beyond 903 K (P_L=81 W). All TiO_2 films showed faceted grains with the columnar cross-section. With increasing T_{dep}, the grain size increased and the column became wider. The high deposition rate (R_{dep}) ranged from 13.04 to 24.84 μm h^{-1}.

1. Introduction

The rutile TiO_2 films are widely investigated because they have many applications such as capacitor, sensors, antireflection coatings and corrosion-resistant barriers. [1–5]. The dielectric constant (ε_r) of rutile TiO_2 crystal is anisotropic and has values of 170 in the *c* direction and 89 perpendicular to the *c* direction, which indicates that TiO_2 film has the possible application to future ultra-large-scale dynamic random access memory (DRAM) [6,7]. TiO_2 films have been prepared by many methods, including sputtering, conventional chemical vapor deposition, sol–gel method, type-casting and laser chemical vapor deposition (LCVD) [8–15]. In our previous work, the rutile TiO_2 film with random orientation was prepared by LCVD with ε_r of 73 [16]. LCVD is considered to be a promising process to prepare high-quality films with controllability of microstructure and orientation at high deposition rate (R_{dep}) [17–20]. It is necessary to investigate the controllability of orientation of the rutile TiO_2 film prepared by LCVD.

In the present study, the TiO_2 films were prepared on Pt/Ti/SiO_2/Si substrate by LCVD, and the effect of laser power (P_L) on orientation and microstructure of TiO_2 films was investigated.

2. Experimental

The TiO_2 films were prepared on Pt/Ti/SiO_2/Si substrates by LCVD with a continuous-wave Nd:YAG laser (wavelength: 1064 nm). A schematic of the laser CVD apparatus has been reported elsewhere [19,20]. The substrate was heated on a hot stage at a pre-heating temperature (T_{pre}) of 773 K. A thermocouple was inserted at the bottom side of the substrate to measure the deposition temperature (T_{dep}). A laser beam, 16 mm in diameter, was introduced through a quartz window to irradiate the whole substrate. The P_L changed from 48 to 98 W. The titanium di-isopropoxy-dipivaloylmethanate ($Ti(Oi\text{-}Pr)_2(DPM)_2$, Toshima Manufactory) precursor was heated at 433 K, and the vapor was carried into the chamber with Ar gas. O_2 gas was separately introduced into the chamber through a double-tube gas nozzle. The total pressure (P_{tot}) in the CVD chamber was held at 600 Pa. The deposition was conducted for 300 s. Details of the deposition conditions are listed in Table 1.

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Table 1
Deposition conditions of TiO_2 film by LCVD.

$Ti(Oi\text{-}Pr)_2(dpm)_2$ evaporation temperature T_{Ti}	433 K
Substrate pre-heating temperature T_{pre}	773 K
Total chamber pressure P_{tot}	600 Pa
Gas flow rate	
Ar gas (FR_{Ar})	8.3×10^{-7} m^3 s^{-1}
O_2 gas (FR_{O2})	1.7×10^{-6} m^3 s^{-1}
Laser power P_L	48–98 W
Deposition time t	300 s
Substrate–nozzle distance	30 mm
Substrate	Pt/Ti/SiO_2/Si ($10\times10\times0.5$ mm^3)

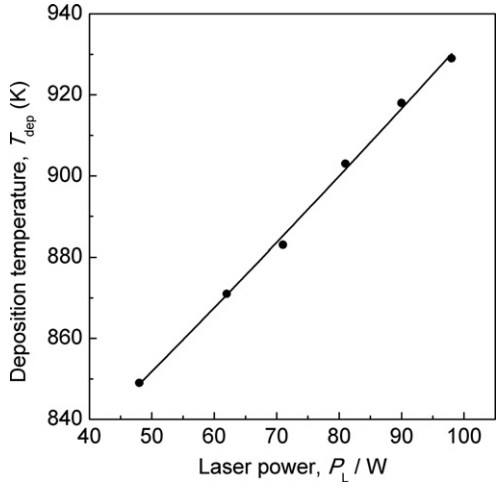

Fig. 1. Effect of P_L on T_{dep} of the TiO_2 films.

The crystal structure of the TiO_2 films was analyzed by X-ray diffraction (XRD, Rigaku RAD - 2C) using CuKα X-ray radiation. The surface and cross-sectional microstructures of the TiO_2 films were observed by a field-effect scanning electron microscope (FESEM, JSM 6335F).

3. Results and discussions

In the LCVD process, T_{dep} can be determined by various parameters, such as P_L, P_{tot}, T_{pre} and precursor evaporation temperature. In this study, only P_L was changed, which indicated that T_{dep} was determined mainly by P_L. The effect of P_L on T_{dep} of the TiO_2 films is shown in Fig. 1. With increasing P_L from 48 to 98 W, T_{dep} monotonously increased from 849 to 929 K.

Fig. 2 shows the XRD patterns of the TiO_2 films prepared by LCVD. The XRD patterns were indexed to the rutile TiO_2 phase (JCPDS 21-1276). At T_{dep}=849 K (P_L=48 W), the rutile TiO_2 film was prepared with strong (110) and (200) peaks. With increasing T_{dep} from 849 to 883 K (P_L=71 W), the intensity of (110) peak increased. At T_{dep}=903 K (P_L=81 W), the (200) peak disappeared. The TiO_2 films showed (110) preferred orientation for T_{dep} beyond 903 K. These results indicated that the orientation of the TiO_2 films could be changed by controllability of T_{dep}.

Fig. 3 displays the typical surface and cross-sectional SEM images of the TiO_2 films. All TiO_2 films consisted of the faceted grains. With increasing T_{dep}, the grain size increased. At high T_{dep}

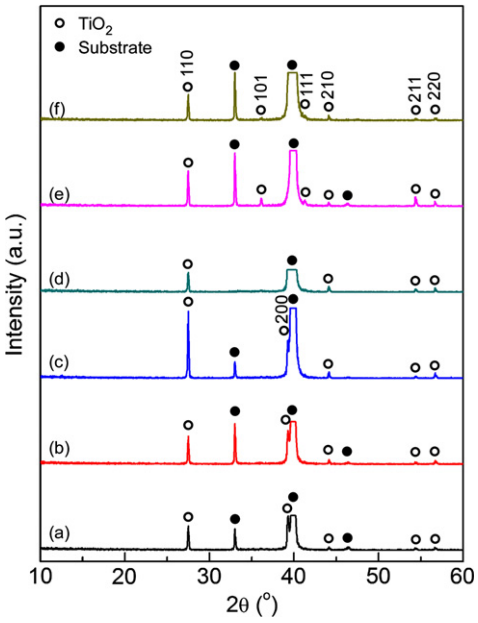

Fig. 2. XRD patterns of the TiO_2 films prepared at different P_L: (a) 48 W, (b) 62 W, (c) 71 W, (d) 81 W, (e) 90 W and (f) 98 W.

(903–929 K), the (110)-oriented TiO_2 films consisted of polyhedrals, which might be explained by the equilibrium shape of rutile TiO_2 crystal based on the *ab initio* total-energy calculations. Ramamoorthy et al. [21] calculated surface energies of the stoichiometric (110), (100), (001) and (011) surfaces of rutile TiO_2 and found that the (110) surface had the lowest energy and the (100) surface was stable with respect to formation of macroscopic (110) facets, which implied that (100) and (110) orientations were preferentially formed. All TiO_2 films had the columnar cross-section, as commonly observed in films prepared by the LCVD method [17–20]. The grains were regularly arranged along the perpendicular direction to the substrate. With increasing T_{dep}, the column became wider. The film thickness ranged from 1.08 to 1.18 μm that indicated that R_{dep} was 13.04–24.84 μm h^{-1}.

Fig. 4 depicts the relationship between R_{dep} and T_{dep} of the TiO_2 films in the Arrhenius format. With increasing T_{dep}, the R_{dep} slightly changed. In the present study, the laser irradiation of the substrate and precursor gases enhanced the chemical reaction and ensured that it is diffusion limited with a high supply rate of precursor gases and high R_{dep} to prepare the TiO_2 films.

4. Conclusions

The single-phase rutile TiO_2 films were prepared on Pt/Ti/SiO_2/Si substrate at high R_{dep} (13.04–24.84 μm h^{-1}) by LCVD. With increasing P_L from 48 to 98 W, T_{dep} monotonously increased from 849 to 929 K. At T_{dep}=849 K (P_L=48 W), the rutile TiO_2 film was prepared with strong (110) and (200) peaks. With increasing T_{dep} from 849 to 883 K (P_L=71 W), the intensity of (110) peak increased. The TiO_2 films showed (110) preferred orientation for T_{dep} beyond 903 K (P_L=81 W). These results indicated that the orientation of TiO_2 films could be changed by controllability of T_{dep}. All TiO_2 films consisted of the faceted grains and the columnar cross-section. With increasing T_{dep}, the grain size increased and the column became wider.