Vol 14 No 3, March 2005
1009-1963/2005/14(03)/0610-05
Chinese Physics
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and IOP Publishing Ltd

Optical properties of $SrTiO_3$ thin films prepared by metalorganic decomposition*

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(Received 8 September 2004; revised manuscript received 12 October 2004)

$SrTiO_3$ thin films were deposited on vitreous silica substrates by metalorganic decomposition (MOD). The films are polycrystalline cubic in structure with the lattice constants of a=0.39nm. Their optical constants (refractive index n and extinction coefficient k) were calculated by the envelope method from the transmittance spectra in the wavelength range of 190nm to 1100nm. The refractive index of the present films is found to be higher than that of the other $SrTiO_3$ films prepared by RF sputtering, sol–gel and chemical vapour deposition. The dispersion of the refractive index in the films follows the single electronic oscillator model with oscillator strength (S_0) of $0.88\times10^{14}\mathrm{m}^{-2}$ and oscillator energy (E_0) of 6.40eV. The optical band gap of the films was estimated to be 3.68eV.

Keywords: optical properties, $SrTiO_3$ thin films, metalorganic decomposition
PACC: 7820D, 7360H, 8115L

1. Introduction

Strontium titanate ($SrTiO_3$), as a member of the perovskite family of compounds, is an important dielectric material. It has been investigated for many years for the prospective applications in microelectronics and optoelectronic fields due to its high dielectric constant, excellent optical properties and simple cubic structure with stable stoichiometry at room temperature. Recently, many researches have been reported on this material. However, most of them mainly focused on the electric properties of $SrTiO_3$.[1−4] Only several reports investigated its optical properties to our knowledge, in which RF sputtering,[5] sol–gel[6] and chemical vapour deposition[7] were employed to prepare the films. As a result of the different preparation methods, the differences in the optical properties of thin films are expected. The metalorganic decomposition (MOD) technique, as one of the solution-based methods for preparing films, has also been widely used in recent years because of the outstanding advantages including low processing temperature, excellent compositional control, homogeneity, ease of fabrication over large areas, and low cost. In this work, we report the preparation of $SrTiO_3$ thin films deposited on vitreous silica substrates by metalorganic decomposition technique. By measuring the transmittance spectra in the wavelength range of 190nm to 1100nm, we investigate their optical constants (n and k), dispersion of the refractive index, and optical band gap.

2. Experimental

Strontium acetate [$Sr(CH_3COO)_2{\cdot}1/2H_2O$] and titanium butoxide [$Ti(OC_4H_9)_4$] were used as the Sr and Ti sources, respectively. Strontium acetate was dissolved in heated glacial acetic acid. An appropriate amount of acetylacetone was added to stabilize the solution before adding the stoichiometric titanium butoxide. The whole solution was refluxed to form a transparent and yellow solution. The concentration of the precursor solution was 0.005M.

The vitreous silica glass with thickness of 0.5mm was used as the substrate. A rapid thermal anneal-

*Project supported by the National Natural Science Foundation of China (Grant Nos 60221502 and 60223006) and Shanghai R&D Foundation for Applied Materials (Grant No 0316).
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ing process realized the crystallization of the films. A single layer of the film was deposited on the substrate using spin coating at 4000rpm for 30s, which then was dried at 180°C for 240s followed by a pre-firing at 380°C for 240s in air. Finally, the film was annealed at 700°C for 240s. The desired thickness of the film was achieved by repeating the spin-coating and heat-treating cycle.

The structure of the films was analysed by x-ray diffraction (XRD) using a Ni-filtered Cu Kα radiation source (D/MAX-RA). The transmittance spectra were studied with a double beam ultraviolet–visible (UV–Vis) spectrophotometer (Perkin Elmer UV–Vis spectrometer Lambda 2S) in the wavelength range of 190–1100nm at room temperature. The transmittance spectrum of uncoated vitreous silica substrate was also measured for a comparison.

3. Results and discussion

X-ray diffraction pattern of $SrTiO_3$ thin film on vitreous silica (Fig.1) shows that the thin film is polycrystalline in structure with the strongest diffraction intensity in (110) line. The broadened peak at the diffraction angle θ of 22° is from the vitreous silica. All the diffraction lines are indexed according to the cubic perovskite structure. The lattice constant were calculated to be a=0.39nm, which is in good agreement with the data prepared by sol–gel.[6]

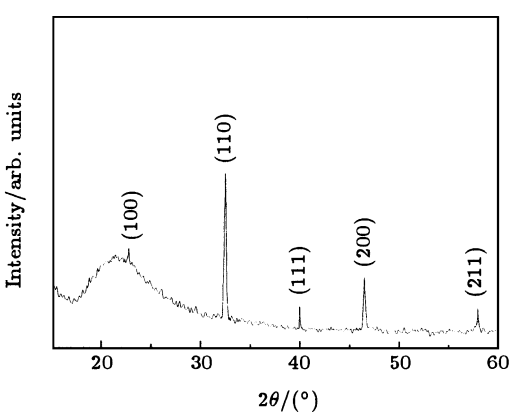


Fig.1. X-ray diffraction pattern of $SrTiO_3$ thin film on vitreous silica prepared by metalorganic decomposition.

Figure 2 shows the transmittance spectrum of vitreous silica substrate coated with $SrTiO_3$ thin film. The transmittance of the uncoated vitreous silica is greater than 93% over the entire spectrum region except for a slight decrease at short wavelengths below 256nm, an effect that is due to light scattering by bubbles inside the vitreous silica.[8] The transmittance of $SrTiO_3$ thin film on vitreous silica is slightly less than that of uncoated substrate. Relatively high transmittance of the film indicates its low surface roughness and good homogeneity.[6] The spectrum can be roughly divided into two regions: a transparent region with the interference pattern and a strong absorption zone. In the region of low absorption, the incident light traverses and reflects in the film several times and produces the interference fringes.

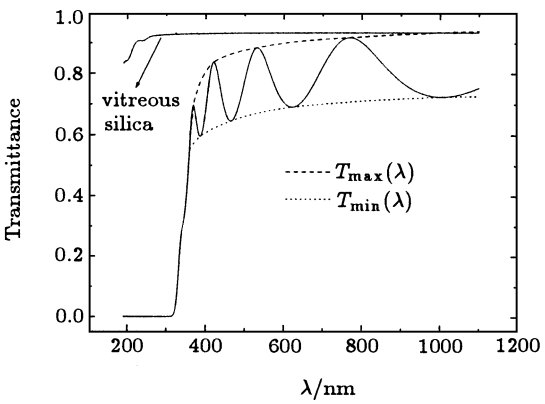


Fig.2. Transmittance spectrum of $SrTiO_3$ thin film on vitreous silica prepared by metalorganic decomposition.

For a weakly absorbing film on a transparent substrate, the optical constants (refractive index n and extinction k) and film thickness can be obtained from the transmittance spectra alone using the envelope method proposed by Manifacier *et al.*[9]

Firstly, considering the thick substrate alone (0.5mm) in the absence of a film, the interference-free transmittance is given by the following well-known expression,[8] where T_s is the measured transmittance:

$$T_s = \frac{2n_s}{n_s^2 + 1} \tag{1}$$

So the refractive index n_s of substrate in the transparent region (for wavelength longer than 256nm) can be obtained from equation (2):

$$n_s = \frac{1}{T_s} + \left(\frac{1}{T_s^2} - 1\right)^{1/2}. \tag{2}$$

In the transparent region of the transmittance spectrum of $SrTiO_3$ thin film on vitreous silica, the transmittance T varies with wavelength λ according to[9,10]

$$T = \frac{16 n_0 n_s n^2 \exp(-\alpha t)}{C_1^2 + C_2^2 \exp(-2\alpha t) + 2C_1 C_2 \exp(-\alpha t)\cos(4\pi n t/\lambda)}, \tag{3}$$

where α is the absorption coefficient, n_0 and n are the refractive indices of air and film, respectively, t is film thickness, and $C_1 = (n + n_0)(n_s + n)$, $C_2 = (n - n_0)(n_s - n)$. The maxima T_{max} and minima T_{min} in the T vs λ plot occur when

$$4\pi n t/\lambda = m\pi, \tag{4}$$

where m is the order number. In the envelope method, both T_{max} and T_{min} are considered as continuous functions of λ. These functions are the envelopes of the maxima and the minima in the transmittance spectrum, as shown in Fig.2. The refractive index n may be computed from the relation

$$n = \left[N + \left(N^2 - n_0^2 n_s^2\right)^{1/2}\right]^{1/2}, \tag{5}$$

where

$$N = \frac{n_0^2 + n_s^2}{2} + 2n_0 n_s \frac{T_{max} - T_{min}}{T_{max} T_{min}}.$$

The film thickness t can be calculated from two maxima or minima using equation (4):

$$t = \frac{M\lambda_1\lambda_2}{2[n(\lambda_1)\lambda_2 - n(\lambda_2)\lambda_1]}, \tag{6}$$

where M is the number of oscillations between the two extrema, λ_1, $n(\lambda_1)$ and λ_2, $n(\lambda_2)$ are the corresponding wavelengths and refractive indices. Knowing n and t, α can be determined from the following equation:

$$\exp(-\alpha t) = \frac{C_1[1 - (T_{max}/T_{min})^{1/2}]}{C_2[1 + (T_{max}/T_{min})^{1/2}]}. \tag{7}$$

Correspondingly, the extinction coefficient k can be calculated using the relation $\alpha = 4\pi k/\lambda$.

Through the above calculation, n, k and t of the film were obtained. The film thickness t was found to be about 383nm, which is in agreement with the value measured by a Rank "Talystep" thickness profiler.

Figure 3 shows the refractive index n of $SrTiO_3$ thin film as a function of wavelength. The dispersion curve of refractive index is fairly flat in the long wavelength region and rises rapidly toward shorter wavelengths, showing the typical shape of a dispersion curve near an electronic interband transition. The refractive index of the present film is found to be higher than that of the other $SrTiO_3$ films prepared by RF sputtering,[5] sol–gel[6] and chemical vapour deposition.[7] It should also be noted that this refractive index is smaller than that of bulk $SrTiO_3$ single crystal.[11] The difference may be related to the packing density p of the film, which can be calculated with the Lorentz–Lorenz relation:[12]

$$p = \left(\frac{n^2 - 1}{n^2 + 2}\right) \Big/ \left(\frac{n_b^2 - 1}{n_b^2 + 2}\right), \tag{8}$$

where n_b is the refractive index of bulk $SrTiO_3$. Taking n=2.158 and n_b=2.394 [11] at 620nm, the value of p is derived to be about 0.90 for the present films. For the films prepared by metalorganic decomposition, some very fine holes emerge inevitably during the process of volatilization and decomposition of organic compositions. This process is similar to that of sol–gel technique. However, the value of p for the present films is higher than that for films prepared by sol–gel (p=0.75).[6]

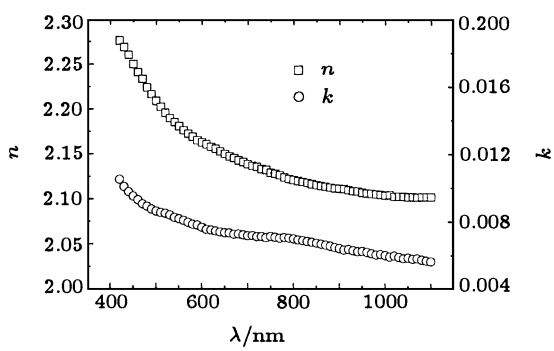


Fig.3. Refractive index n and extinction coefficient k of $SrTiO_3$ thin film on vitreous silica as functions of wavelength.

Figure 3 also shows the variation of extinction coefficient k of $SrTiO_3$ thin film with wavelength. The extinction coefficient increases gradually with the shortening of wavelength. All the values of k are very small (lower than 0.011 in the transparent region), which allows the light wave to traverse the sample several times and subsequently produce the interference fringes in the transmittance curve (Fig.2). It should be noted that the light-intensity loss from the back surface of the substrate was not taken into account in the envelope method.[9] Therefore, the calculated k value actually included the total optical losses caused by both absorption and scattering.

The dispersion data of the refractive index indicate that the interband transition region follows a single electronic oscillator model. Therefore, the refrac-

tive index in the low absorption region should follow the relation[10]

$$n(\lambda)^2 - 1 = \frac{S_0\lambda_0^2}{1-(\lambda_0/\lambda)^2}, \quad (9)$$

where S_0 is the oscillator strength, and λ_0 is the average oscillator position. For analysing the above formula in the present case, the curve of $1/(n^2\text{-}1)$ vs $1/\lambda^2$ has been plotted in Fig.4. The data fit to a straight line indicating the applicability of Sellmeier's dispersion formula for our $SrTiO_3$ thin films.[8] The values of S_0 and λ_0 are estimated from the slope $(-1/S_0)$ and the infinite wavelength intercept $(1/S_0\lambda_0^2)$. The oscillator energy E_0 is given by$E_0 = hc/e\lambda_0$ (c is the light velocity, h is Plank's constant, and e is the charge of the electron). The calculated parameters S_0, λ_0, E_0, and the refractive index dispersion parameter E_0/S_0 are listed in Table 1 along with those for bulk $SrTiO_3$ and the film prepared by sol–gel. The S_0 parameter of our resultant $SrTiO_3$ thin film is higher than that of the film prepared by sol–gel,[6] but slightly lower than that of the bulk.[13] The parameter E_0 is higher than that of films prepared by sol–gel[6] and that of the bulk.[13] This reveals that different deposition techniques can affect the electronic structure in the films.

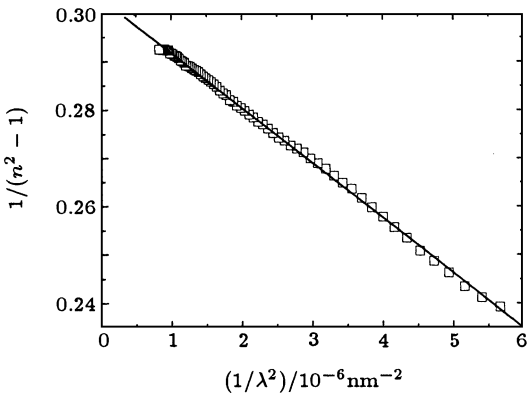


Fig.4. Experimental values and single electronic oscillator model fit for $SrTiO_3$ thin film on vitreous silica.

Table 1. Sellmeier's dispersion parameters for $SrTiO_3$ thin films prepared by MOD and sol–gel techniques as well as the bulk $SrTiO_3$.

Samples	λ_0/nm	$S_0/10^{14}\mathrm{m}^{-2}$	E_0/eV	$(E_0/S_0)/10^{-14}\mathrm{eV\cdot m}^2$
MOD (present work)	194	0.88	6.40	7.27
Sol–gel [6]	218	0.43	5.69	13.23
Bulk $SrTiO_3$ [13]	216	0.89	5.74	6.5

Near the absorption edge or in the strong absorption zone of the transmittance spectra, the envelope method is not applicable. In this case, transmittance T varies exponentially with the absorption coefficient α, therefore α may be determined from the relation[10]

$$T = A\exp(-\alpha t), \quad (10)$$

where the parameter A is found to be nearly equal to unity. For photon of energy $h\nu$ falling on the material and assuming direct transition between the valance and conduction bands, the absorption coefficient is related to the band gap E_g in the following manner:[8]

$$(\alpha h\nu)^2 = C(h\nu - E_g), \quad (11)$$

where C is a constant. The E_g value was estimated to be 3.68eV by extrapolating the linear portion of $(\alpha h\nu)^2$ vs $h\nu$ plot to $(\alpha h\nu)^2$=0 in Fig.5. This value is slightly higher than that for the films prepared by sol–gel (3.62eV),[6] which further reveals the effect of the deposition techniques of films on the optical properties. It should be noted that the E_g value for the present film is higher than that for the bulk $SrTiO_3$ (3.22eV),[14] which may be attributed to the stress in the film due to the difference in the thermal expansion coefficients of the substrate and the $SrTiO_3$ film.[6,10]

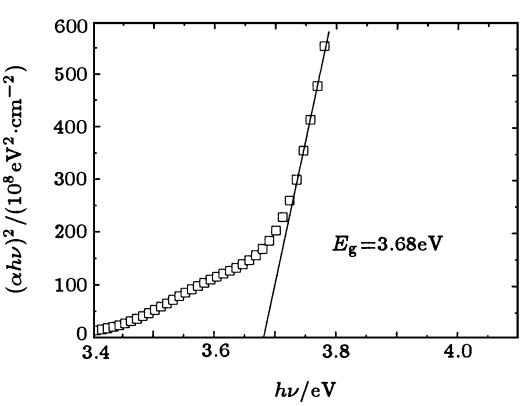


Fig.5. Plot of $(\alpha h\nu)^2$ vs photon energy $h\nu$ for $SrTiO_3$ thin film on vitreous silica. The optical band gap is deduced by extrapolating the straight line to $(\alpha h\nu)^2$=0.

4. Conclusion

In summary, $SrTiO_3$ thin films have been deposited on vitreous silica substrates by metalorganic decomposition. X-ray diffraction shows that they are

polycrystalline in structure with the lattice constant of a=0.39nm. The envelope method was used to calculate their optical constants (n, k) from the transmittance measurements. The refractive index of the present films is found to be higher than that of the other $SrTiO_3$ films prepared by RF sputtering, sol–gel and chemical vapour deposition. The dispersion of the refractive index in films follows the single electronic oscillator model. Using this model, the values obtained for the oscillator strength (S_0) and the oscillator energy (E_0) are $0.88\times10^{14}\mathrm{m}^{-2}$ and 6.40eV, respectively. The optical band gap of the films estimated by assuming direct transition (between the valance and conduction bands) is 3.68eV.

Acknowledgements

The authors would like to thank Dr J. Chen and Dr Z. M. Huang for their technical assistance.

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