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INDUCED CRYSTALLIZATION IN CW LASER-
IRRADIATED SOL-GEL DEPOSITED TITANIA FILMS

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INDUCED CRYSTALLIZATION IN CW LASER-IRRADIATED SOL-GEL DEPOSITED TITANIA FILMS

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Abstract

Isothermal annealing of amorphous TiO_2 films deposited from acidic sol-gel precursor solutions results in film densification and concomitant increase in refractive index. Subsequent heating above 300°C leads to irreversible transformation to an anatase crystalline phase. Similar phenomena occur when such amorphous films are subjected to focused cw laser irradiation. Controlled variations in laser fluence are used to densify or crystallize selected regions of the film. Low fluence conditioning leads to the evolution of a subtle nanograin-size morphology, evident in AFM images, which appears to retard subsequent film crystallization when such regions are subjected to higher laser fluence. Time-resolved Raman spectroscopy has been used to characterize irradiated regions in order to follow the crystallization kinetics, assess phase homogeneity, and evaluate accompanying changes in residual film stress.

Introduction

A rapid, inexpensive procedure for the deposition of metal oxide coatings is based on the sol-gel processing technique. In this method, a precursor reagent, usually the alkoxide of the target metal oxide, is dissolved in a suitable reagent where hydrolysis and condensation reactions are controlled in order to develop the oxide phase and accompanying microstructure.¹⁻⁴ Amorphous films are formed readily by means of spin-casting or dip-coating cleaned substrates. Such films usually exhibit refractive indices much lower than amorphous coatings deposited using the more energy intensive PVD methods and film adhesion to the substrate appears to be somewhat poorer. However, adhesion can be improved markedly through solution processing at relatively low pH.⁵ Deposition of low index coatings using the sol-gel process offers the possibility for the production of spatially-resolved dense coating regions through subsequent thermal processing routes.

Isothermal heating of amorphous sol-gel titania films above 300°C results in an irreversible transformation to the crystalline anatase phase characterized by a spheroidal grain morphology with grain sizes less than 100 nm.⁶ Film densification accompanies this transformation and intact films are produced provided that the overall thickness is kept to less than 500 nm. The growth rate of evolved crystallites is retarded owing to diminished transport of the amorphous matrix to the densified nucleation center and is well-represented by a modified Avrami equation with a critical exponent on the order of two.⁶ The magnitude of residual stress in these films and how it varies during crystallization has been followed in real time by means of Raman scattering measurements.⁷ This previous work demonstrated that simultaneous

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measurement of two Raman mode frequencies is sufficient to uniquely determine both temperature and residual stress as the amorphous film crystallizes. Since time-resolved Raman measurements can be carried out on very short time scales, this method is appropriate for following crystallization phenomena in amorphous films subjected to rapid step increases in temperature.

Focused laser radiation offers the capability for producing rapid heating of films as well as the possibility for imprinting surface regions of variable refractive index. In work reported here, irradiation of amorphous sol-gel deposited films with a visible cw laser results in localized densification and crystallization at the irradiation sites. A critical laser fluence must be exceeded before crystallization can occur. Time-resolved Raman measurements acquired during sample irradiation are used to characterize surface temperature, the residual stress state of the film and how it evolves in time. Ongoing work involves applications of this technique for writing micrometer size images into refractory films deposited on silica or silicon substrates.

Experimental

Sol-gel titania films were prepared from highly acidic ethanol solutions of the titanium ethoxide precursor.⁷ Homogeneous films were formed on silica or silicon(100) cleaned substrates at room temperature by spin casting at rates between 1200 and 1700 rev·min⁻¹ for 60 s. Film thicknesses ranged from 200 to 1200 nm as determined from uv-vis-ir transmission measurements⁸ and ellipsometry (632.8 nm and 70° incidence angle). Refractive indices averaged about 1.65 immediately after casting, and were found to increase somewhat with time at room temperature or during gentle heating.

Isothermal heating of films to 120°C was achieved by means of a heat lamp located 25 cm above the coated substrates. Heating to higher temperatures involved the use of a muffle furnace or a resistively wound optical furnace for the *in situ* Raman measurements.⁶ Surface morphology after heating was characterized by means of Transmission Electron Microscopy and Atomic Force Microscopy.^{6,9}

Laser heating involved imaging cw all-line emission from an Ar-ion laser onto the sol-gel coated substrate by means of an aberration-corrected 10x microscope objective having a small numerical aperture. Beam diameters were estimated at 20 μm. Under these conditions, laser fluences approaching several megawatts per cm² could be achieved. Film irradiations were performed at a number of fluences ranging from 0.1 to 5 MW·cm⁻² and over times ranging from a few seconds to minutes.

Spatially resolved Raman measurements of the laser irradiated regions were collected using an optical microscope interfaced to the entrance port of a Spex triple spectrometer. Spectra were excited using 100 mW of 514.5 nm argon ion laser radiation focused onto the sample by means of a 40x objective. Raman scattering was collected in a backscattering geometry. These conditions did not lead to densification or crystallization of the films during measurement. At significantly higher laser fluences through the microscope, changes to the film became evident.

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Results

The refractive index of amorphous sol-gel deposited titania films increases from 1.52 to 1.76 over a period of 60 hours upon drying at room temperature. An increase in index to about 2.00 is observed after films have been heated to temperatures near 100°C. Extinction coefficients nearly double as the films densify and contract to about half of their original as-deposited thickness. These results are in agreement with those of Thomas, *et al*, who observed similar effects in sol-gel films upon mild heat treatment or exposure to uv light.¹⁰ The nature of the substrate has little effect on these changes which are seen in films deposited on silica as well as Si(100) surfaces.

Isothermal heating to temperatures in excess of 300°C leads to irreversible crystallization of the amorphous film to an anatase crystal phase. The kinetics of the transformation are controlled by the length of solution equilibration time prior to casting, drying time and temperature, and the substrate temperature during deposition.^{6,11} The spheroidal microstructure which evolves (Fig. 1) is characterized by uniform close packed crystal grains having diameters less than 100nm. In general, the rate constant for the fraction of transformed material, F , is described by a modified Avrami equation (eqn. 1) where the temperature dependent rate constant for crystallization is k and the critical exponent, c , describes the crystallite habitat and includes mass transport effects.⁶ Critical exponents are on the order of 2. The activation energy for crystallization is 34 kcal/mole.

$$F = 1 - \exp(-k \cdot t^c) \quad (1)$$

Fig. 1 TEM image of an 80nm thick anatase film removed from the silica substrate. Spheroidal grains average 50nm in diameter.

The two types of phenomena, conditioning and crystallization, illustrated above also are seen when amorphous as-deposited titania films are subjected to cw laser irradiation. For fluences below 1 MW.cm⁻², films were observed to densify accompanied by increases in both refractive index and extinction coefficient. At fluences exceeding this threshold, irreversible transformation to the anatase crystalline phase was observed. An increase in index to 2.40 was determined from ellipsometry measurements. Points A and B in Fig. 2 refer to regions of the film which have been conditioned and which have been irreversibly transformed to the anatase phase. Irradiation at fluences above 3MW.cm⁻² led to catastrophic damage to the film which included material ablation, and recrystallization of the metastable amorphous and anatase phases to the rutile crystalline phase. The presence of multiple phases is readily discerned from Raman microprobe measurements of the damaged area.¹²

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Fig. 2 Spatially resolved ellipsometric measurements of cw laser irradiated titania sol-gel coatings. (A) Conditioned region. (B) Transformed region.

Under irradiation conditions where the film does not suffer catastrophic damage, time-resolved Raman Spectroscopy has been used to follow induced crystallization phenomena. Fig. 3 illustrates the kind of information such measurements provide.

Fig.3 Laser-induced crystallization of TiO_2 films on SiO_2 . (a) Time-dependent intensity increase of the 143 cm^{-1} E_g anatase mode. (b) Measured line frequency shifts for the two strong E_g modes in anatase. (c) Associated film temperature and residual film stress after reference 7.

At a fluence exceeding $1 \text{ MW}\cdot\text{cm}^{-2}$, but less than $2 \text{ MW}\cdot\text{cm}^{-2}$, the irradiated region completely transforms to the anatase phase in about ten minutes and the crystallite ingrowth rates are described by eqn. 1 with a critical exponent of 2. Frequencies for the two strongest anatase modes associated with each intensity measurement vary similarly in time and are used to determine film temperature and residual stress during crystallization by means of the contour analysis method developed previously.⁷

The film temperature in the irradiated region increased to over 500°C and then gradually decreased to a steady state value of about 425°C . Relaxation of residual film compressive stress by about 4 kbar also was seen. Similar results were found for films subjected to fluences between 2 and $3 \text{ MW}\cdot\text{cm}^{-2}$. However, complete crystallization was completed within a matter of seconds. Fig. 4 illustrates the observed time dependence of the 143 cm^{-1} mode intensity and frequency. The film reached a maximum temperature of 550°C and then cooled to a steady state value of about 475°C . Residual stress also was found to relax by about 5 kbar.

Fig. 4 Laser-induced crystallization of TiO_2 films on SiO_2 . Changes in 143 cm^{-1} mode frequency and intensity.

Discussion

Modification to film optical properties and thickness during drying at moderate temperatures likely results from solvent and water loss. This effectively raises the glass transition temperature of the amorphous film and thereby acts to retard crystallization when films are heated to higher temperatures. During this *annealing* process, the extended network structure of the amorphous film will relax to a lower energy state, forming an extended network structure more resistant to crystallization. Under laser irradiation at relatively low fluences, the irradiated region densifies in analogy to thermal conditioning, and this treatment appears to retard crystallization of these regions at higher fluences when compared with unconditioned areas of the film.

At fluences beyond a critical threshold, irreversible crystallization of amorphous titania films ensues. Absorption of the energy leads to marked increases in film temperatures within the footprint of the focused laser beam. In these regions, large increases in refractive index are observed and are characteristic of the anatase phase. Transformation rates depend on laser fluence. Beyond a critical threshold, catastrophic damage to the film results and transformation to a rutile crystalline phase is indicated from Raman microprobe measurements within the damage region.

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Conclusions

Irradiation of sol-gel deposited titania films at increasing laser fluence has been shown to lead to (i) conditioning with associated increased index, (ii) crystallization with associated index increase, and (iii), catastrophic damage depicted by material ablation and the presence of multiple crystalline phases. Time-resolved Raman measurements acquired during irradiation verify localized temperature increases and relaxation in residual compressive film stress. Results suggest that image inscription into amorphous sol-gel deposited films is possible by means of controlled laser irradiation. The inscribed images will show marked variation in refractive index when compared with unirradiated regions of the film.

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