Ion Beam Processing of Nanocluster-containing Thin Films

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Abstract

We report the use of ion beam processing to fabricate thin films of metal or semiconductor nanoclusters in dielectric matrices. Thin films of this kind have been shown to have high values of third order nonlinear optical (NLO) constants and exhibit photoluminescence (PL).

Metal nanocluster thin films consisting of clusters 5-30 nm in size embedded in an active metal oxide matrix were deposited by ion beam assisted deposition (IBAD) by co-evaporation of two metals, one more highly reactive toward oxygen than the other, with O_2^+ ion bombardment. Values of $X^{(3)}/\alpha$ for the IBAD films were as good as those reported for ion implanted films and, for optimized IBAD deposition and annealing conditions, the values were superior. The advantages of the IBAD method for fabricating third order NLO films include the ability to deposit films with greater active region thicknesses and higher nanocluster densities as well as the fabrication of a range of metal nanocluster/dielectric combinations and the variation of cluster density by adjusting either deposition rate or ion bombardment conditions.

Introduction

There has been much interest recently in the optical properties of nanocluster composites. Metal nanocluster composites consisting of small (30 nm) metal clusters in a dielectric matrix have exhibited picosecond nonlinear response times with effective third order susceptibilities several hundred times larger than those of colloidal melt glasses.[1,2] Metal nanocluster composites have typically been formed by ion implantation of metals such as Cu and Au into glass substrates.[1, 3-7] In addition, the discovery of PL in porous Si [8] has led to a great deal of attention being directed at the fabrication of Si and other semiconductor nanocrystals for the purposes of studying the effect of carrier confinement. Si nanocrystals have been fabricated by anodic etching [8], selective size precipitation [9], spark erosion [10], and chemical vapor deposition,[11] in addition to ion implantation. [12]

Ion beam assisted deposition (IBAD) is an alternative processing method for such nanocomposite structures.[13, 14] IBAD offers a number of potential advantages over other methods for introducing nanoclusters to a dielectric matrix. Simultaneous deposition of the oxide and the metal allows deposition of cluster-containing films of uniform composition with respect to the size and density of clusters. There are no practical limits to film thickness other than deposition time and very high concentrations of metal clusters are possible. Furthermore, IBAD films are typically of high density.

In this paper we report our observations on the use of ion beam processing to deposit nanocluster films with desirable NLO or PL properties.

Experimental Procedures

The thin films were deposited by IBAD in a multihearth vacuum chamber with a base pressure of 5×10^{-9} mmHg. For metal nanocluster films, two metals, one significantly more active toward oxygen than the other, were deposited simultaneously under bombardment with O_2^+ ions. The active metal was oxidized by the ion beam to form the dielectric matrix, while the less active metal (hereafter referred to as the "noble" metal) formed the metal clusters. For the Si-SiO_2 films, silicon and silica were coevaporated from two e-beam hearths. To observe the effects of ion beam processing, some of the Si-SiO_2 films were exposed to an Ar^+ ion beam during evaporation. The metal or semiconductor nanocluster films were deposited simultaneously on Si and SiO_2 substrates. The substrate temperatures ranged from room temperature to 730℃. Post-deposition anneals were conducted in vacuum or flowing gas (O_2 or N_2) at temperatures between 500 and 900℃.

Results

Metal Nanocluster Films

Films containing metal nanoclusters all

showed a strong linear absorption at the wavelength of the surface plasmon resonance for the metal. The intensity of the absorption was dependent on the size and concentration of the metal clusters and could be modeled according to Mie Theory for scattering and absorption, as has been shown in detail previously. [13] The intensity of the linear absorption increased with annealing due to the ripening of the clusters during the anneal. There was not a substantial effect of deposition

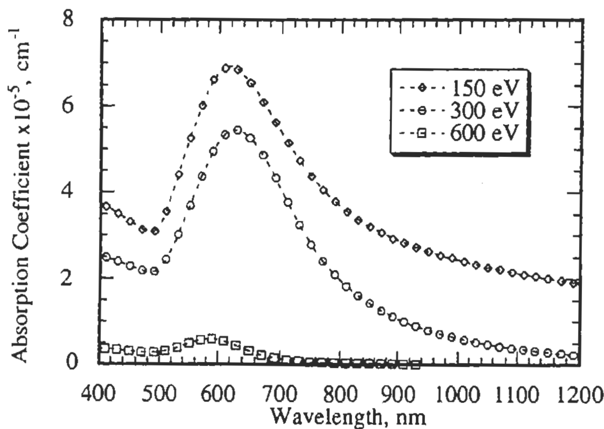


Fig.1 Optical absorption data for three annealed Au/Nb_2O_5 films deposited with the same Au and Nb evaporation rates but at three different ion energies: 150, 300 and 600 eV. The evaporation rates for Au and Nb were 0.04 and 1.2 nm s-1. After deposition, the films were annealed for 10 min in O_2 at 600 ℃.

temperature on the size of nanoclusters. The clusters in films deposited at 730℃ were a few nm larger than those in films deposited at room temperature.

The concentration of nanoclusters was a function of the relative rates of evaporation of the active and noble metals as well as the ion beam energy. Higher concentrations gave

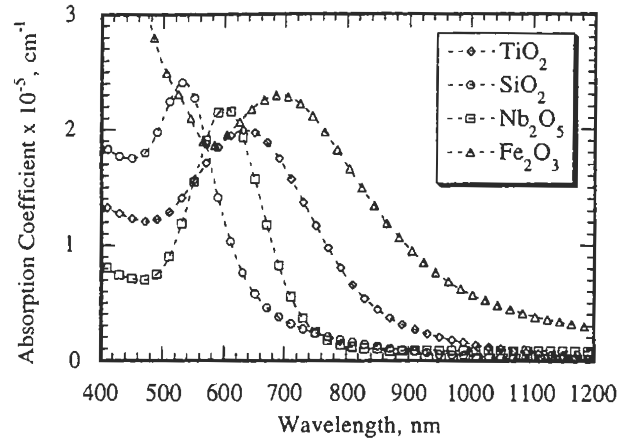


Fig.2 Linear absorption curves for IBAD films of Au clusters in a variety of dielectrics.

stronger linear absorption. The correlation of linear absorption with ion beam energy for the example of Au clusters in Nb_2O_5 is shown in Fig. 1. Fig. 1 plots the optical absorption data for three annealed films deposited with the same Au and Nb evaporation rates but at three different ion energies: 150, 300 and 600 eV. RBS analysis of the films showed less Au in the samples deposited at higher energies. This behavior may be explained by preferential sputtering of Au from the films during deposition at the higher ion energies.

The wavelength of linear absorption was a function of the combination of metal and dielectric in the films.[14] Fig. 2 shows linear absorption curves for IBAD films of Au clusters in a variety of dielectric matrices. For a given metal/dielectric combination, the wavelength of the absorption peak could be shifted slightly by means of adjusting the ion beam energy, but the peak could not be shifted significantly.

Measurement of NLO properties showed very high values of $\chi^{(3)}$, especially for annealed samples. For Au nanoclusters in Nb_2O_5,

Table 1: Wavelength of IR absorption for the asymmetric stretching mode of Si-O bonds and atom fraction, x, of O in SiO_x, as calculated from IR measurements and as measured by RBS, and the atom fraction of H in SiO_x films deposited by IBAD by coevaporation of Si and SiO_2 under bombardment with Ar^+ ions at 100 eV and 35 mAcm^{-2}.

Si/SiO_2 Arrival Rate Ratio	Frequency of IR absorption (cm^{-1})	x in SiO_x, as calculated from IR data	x in SiO_x, as measured by RBS	y in SiO_xH_y, as measured by ERD
0.2 (no beam)	1063	1.75	2.05	0.135
0.4 (no beam)	1048	1.52	1.57	0.15
0.2 (w/ beam)	1056	1.65	1.65	0.09
0.4 (w/ beam)	1041	1.45	1.13	0.026

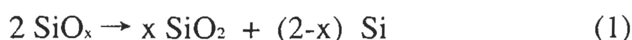
a value for $|\chi^{(3)}xxxx|$ as high as 7×10^{-8} esu was measured.[13] The figure of merit for these materials is $\chi^{(3)}/\alpha$, however. The corresponding value of $\chi^{(3)}/\alpha$ was 3.3×10^{-13}, a less impressive number due to the strong linear absorption, α, of the Au clusters. Measurement of the third order nonlinear susceptibility at wavelengths remote from the surface plasmon resonance where the linear absorption coefficient was not as strong did not show high values of $\chi^{(3)}/\alpha$.

Semiconductor Nanocluster Films

The stoichiometry of $Si\text{-}SiO_2$ films was a function of bombardment with Ar^+ ions.

Pai et al. [15] demonstrated that the Si-O IR stretching mode at 1075 cm^{-1} shifts to lower frequencies with decreasing x in SiO_x mixtures. IR spectra and RBS analysis showed that films deposited by coevaporating Si and SiO_2, with and without IBAD, tended to be substoichiometric (i.e., x<2), as shown in Table 2, which tabulates the frequency of this IR signal, the atom fraction, x, of O in SiO_x as calculated from the IR measurements and as measured by RBS, and the atom fraction of H in these films, as measured by elastic recoil detection (ERD). The effect of the ion beam bombardment was to decrease the value of x by a small amount relative to that observed for films deposited at the same Si evaporation rate without ion bombardment. The most dramatic effect of ion bombardment, however, was the reduction in the hydrogen content of the films. Although care was taken to bake out the vacuum chamber prior to depositions, some hydrogen was found in all the films. The nature of the hydrogen incorporation into the films remains unclear. Neither Si-H bands nor absorptions attributable to water were observed in the IR spectra.

Annealing of pure SiO_x or $Si\text{-}SiO_x$ films deposited with or without ion beam bombardment resulted in the formation of Si particles. According to the results of Nesbit [16], this reaction takes place according to,



$$2\,SiO_x \rightarrow x\,SiO_2 + (2-x)\,Si \qquad (1)$$

PL spectra taken from SiO_x and $Si\text{-}SiO_x$ samples deposited with and without ion bombardment showed a weak PL signal at 550 nm, which has been attributed by Min et al. [17] to defects. $Si\text{-}SiO_x$ samples deposited without ion bombardment showed an additional broad, low intensity PL signal at ~700 nm. $Si\text{-}SiO_x$ samples deposited with ion bombardment showed a similar signal at a somewhat higher wavelength (~740 nm). As shown in Fig. 3, annealing of these samples in a mixture of 20% oxygen in a balance of nitrogen resulted in an increase in intensity and a shift to higher wavelengths of the PL signals from the samples deposited both with and without ion bombardment. The intensities of the PL signals from the IBAD samples were much lower than for the evaporated samples. As shown in Table 1, the IBAD samples had much lower concentrations of hydrogen. Passivation of the films by hydrogen may account for the differences in PL intensity, as suggested by Min, et al. [17]

Characterization of the microstructure of the Si nanocluster films by transmission electron microscopy (TEM) showed that while the size of nanoparticles was about the same (1-4 nm), the ion beam had a noticeable effect on the distribution of particles and the morphology of the matrix. The matrices of both evaporated and IBAD films were amorphous, but evaporated films had a cellular structure (cell size of ~0.1μ m in diameter), while IBAD films were homogeneous. Particles comprised about 50% of the IBAD films by volume, but only about 5% of the evaporated films. Evaporated films that were annealed in nitrogen showed cluster sizes that depended on the Si/SiO_2 arrival rate. For a relative arrival rate of 0.4, the clusters were 1.4 -4.0 nm, whereas for an arrival rate of 0.8, the clusters were 10 nm.

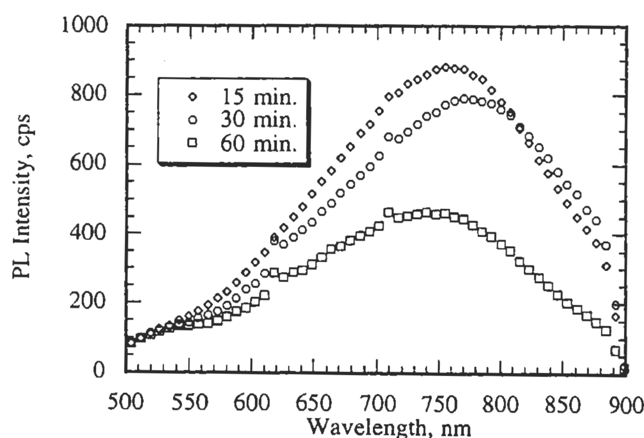


Fig.3 Photoluminescence spectra for a Si-SiOx film deposited by IBAD with a Si/SiO_2 arrival rate ratio of 0.8 annealed in a gas mixture consisting of 80/20 nitrogen/oxygen at 900℃ for 15, 30 and 60 minutes.

A correlation between the size of nanoparticles and the intensity of the PL signal was observed. As shown in Fig. 3, a series of annealing experiments with a Si-SiO_x film deposited with a high Si/SiO_2 arrival rate ratio of 0.8 illustrated this effect. Annealing in oxygen at 900℃ for various times resulted in continual decrease in the PL signal. The likely effect of the high temperature anneal in oxygen was to oxidize the Si particles, thereby shrinking them in size.

Discussion

IBAD is clearly an effective, flexible technique for the deposition of thin films of metal nanoclusters in dielectric matrices. High concentrations of metal clusters can be introduced and the distribution of clusters with respect to both size and shape is uniform. A variety of metal/dielectric combinations can be deposited. However, while small shifts in the wavelength of linear absorption can be induced by ion bombardment, the absolute utility of metal nanocluster films as NLO materials is limited by the fact that the nonlinearities are resonance-enhanced and the strong linear absorption of the metal clusters at the wavelength of the surface plasmon resonance leads to lower values of $\chi^{(3)} / \alpha$ than are achievable in semiconductor systems. IBAD films of metal nanoclusters may ultimately be more useful in optical storage media applications in which the bleaching characteristics that have been observed [18] could be exploited. In this case, the ability to deposit thick films will be an advantage.

The potential of IBAD for deposition of semiconductor nanocluster films with measurable PL is starting to be exploited. IBAD clearly increases the concentration of clusters in the films and influences the hydrogen content, which seems to be related to the PL intensity. Experiments are presently underway to determine if oxidation and passivation with hydrogen can be accomplished in situ during IBAD to optimize the PL characteristics.

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