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ION-IRRADIATION-INDUCED DENSIFICATION OF ZIRCONIA SOL-GEL THIN FILMS

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ABSTRACT

We have investigated the densification behavior of sol-gel zirconia films resulting from ion irradiation. Three sets of films were implanted with neon, krypton, or xenon. The ion energies were chosen to yield approximately constant energy loss through the film and the doses were chosen to yield similar nuclear energy deposition. Ion irradiation of the sol-gel films resulted in carbon and hydrogen loss as indicated by Rutherford backscattering spectrometry and forward recoil energy spectroscopy. Although the densification was hypothesized to result from target atom displacement, the observed densification exhibits a stronger dependence on electronic energy deposition.

INTRODUCTION

Sol-gel synthesis has the potential of producing dense ceramic thin films on almost any substrate[1]. A shortcoming, however, of the sol-gel technique is that many substrates cannot tolerate the high temperatures (700-900 °C) necessary for processing.

Shacham-Diamand et. al. have shown that sol-gel silica films densify during ion irradiation close to room temperature[2]. We have previously quantified the same effect on sol-gel zirconia thin films[3,4]. We have characterized densification of the films as the combined observations of chemical, compositional, and physical changes in the films. The chemical changes were noted as the attenuation of peaks characteristic of hydroxyl (-OH) and alkoxy (-OR) groups measured via Fourier transform infrared spectroscopy. Compositional changes consisted of the loss of volatile species of carbon, hydrogen, and excess oxygen, in the form of -OH and -OR groups as measured by Rutherford backscattering spectrometry (RBS) and hydrogen forward recoil energy spectroscopy (FRES). The physical changes were observed via ellipsometry as a decrease in thickness of the films with increasing dose. We have also previously demonstrated that the observed densification is not a result of ion beam heating as an implanted thick film exhibited densification only within the range of the ion and its recoils [4]. As such we have attributed the observed densification to a combination of electronic and nuclear energy loss modes.

In this paper we present the results of an investigation directed towards the determination of the dominant energy loss mode, electronic or nuclear, of ion-beam-induced densification of sol-gel zirconia thin films. Here we characterize densification by the loss of hydrogen and carbon in the films. As structural rearrangement is paramount to sol-gel film densification under conventional sintering conditions, it was supposed that nuclear energy loss, through target atom displacements, is primarily responsible for ion-beam-induced densification. To test this hypothesis, we have ion-beam densified thin films of sol-gel zirconia via implantation with one of three noble gases, each to doses necessary to yield equivalent nuclear energy deposition in the films. The doses were calculated according to equation (1).

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$$\frac{E_n}{\text{atom}} = \phi \times \varepsilon_n = \text{constant} \tag{1}$$

where $\frac{E_n}{\text{atom}}$ = energy deposited into nuclear processes/atom

ϕ = implanted dose,

ε_n = nuclear stopping cross-section.

The nuclear stopping cross-section was determined using TRIM [5] for the incident ion energy. Should the densification be caused primarily by nuclear energy loss modes then it is expected that similar quantities of nuclear energy deposition should yield similar densification as quantified by hydrogen and carbon loss. Specifically, we arrive at a densification fraction for the hydrogen content using equation 2.

$$f = \frac{(Nt)_{o,H} - (Nt)_H}{(Nt)_{o,H} - (Nt)_{f,H}} \tag{2}$$

where $(Nt)_{o,H}$ = areal density of H in an as-deposited film

$(Nt)_{f,H}$ = areal density of H in an annealed film

$(Nt)_H$ = areal density of H in an implanted film

EXPERIMENTAL

Sample preparation

A zirconia sol with mole ratios of Zr:CH_3COOH:n-$CH_3CH_2CH_2OH$ equal to 1:16.5:15.7 was prepared by dissolving zirconium(IV) propoxide in glacial acetic acid and 1-propanol as described previously by Pascual et al.[6]. Films were deposited by spinning the sol at 2000 rpm onto single crystal silicon wafers of (100) orientation that were previously cleaned with acetone. Deposition was followed by a heat treatment in a furnace at approximately 100 °C for 30 minutes.

Samples were implanted at the Ion Beam Materials Laboratory at Los Alamos National Laboratory. The beam current density was approximately 1.0 $\mu A/cm^2$ to keep the target temperature below 100 °C. Twelve samples were implanted at room temperature and at a base pressure of 7×10^{-4} Pa according to Table I.

Table I. Ion beam processing parameters

Ion	Energy (keV)	Dose (atoms/cm^2)	Dose (atoms/cm^2)	Dose (atoms/cm^2)	Dose (atoms/cm^2)
Ne^{++}	280	2.65×10^{15}	-	-	-
Ne^{+}	140	-	3.63×10^{16}	1.82×10^{17}	3.64×10^{17}
Kr^{++}	280	1.77×10^{14}	1.77×10^{15}	8.85×10^{15}	1.77×10^{16}
Xe^{++}	280	1.00×10^{14}	1.00×10^{15}	5.00×10^{15}	1.00×10^{15}

The doses were chosen to yield similar nuclear energy deposition in the films as described by equation 1. And as our previous investigations have shown densification for 280 keV implanted Xe, similar beam parameters were chosen here. Neon was implanted at two different energies because of exceedingly low beam currents of the doubly charged specie. During implantation the sample stage temperature did not rise above 50 ^oC.

For comparison purposes a sample was annealed at a heating rate of 15 ^oC/min. to a temperature of 750 ^oC where it was held for one hour.

Analytical techniques

Ion beam analysis was performed at the Ion Beam Materials Laboratory at Los Alamos National Laboratory. RBS and FRES were performed using 2.4 MeV $^4He^+$ particles produced by a 3 MV tandem accelerator. The accelerator has a base pressure of 7×10^{-4} Pa. The $^4He^+$ beam current was 40 nA and the average spot size was .001 x .001 m. The resolution is 18 keV and 70 keV for RBS and FRES, respectively.

Spectra were taken with the sample tilted to 75^o while the detector was placed at 13^o and 150^o with respect to the incoming beam for RBS and FRES, respectively. The tilt angle was selected to enhance depth resolution.

Additional RBS measurements were taken at 3.6 MeV using the same accelerator in order to take advantage of the increased scattering cross-section of carbon due to an $^{12}C(\alpha,\alpha)^{12}C$ resonance. During these analyses the samples were tilted to 45^o to enhance depth resolution.

Carbon and hydrogen contents in the films were calculated via peak area measurement with background subtraction from a suitable standard according to techniques described elsewhere[7]. The error in the calculated areal densities was calculated not to be greater than 5 percent.

RESULTS/DISCUSSION

Figure 1a shows representative backscattering spectra for the set of samples implanted with krypton. Figure 1b depicts the corresponding FRES spectra taken simultaneously with the RBS spectra. Most notable in figure 1a is the increasing height and decreasing width of the zirconium peak (starting at channel 790) with increasing dose. The change in the zirconium peak with dose results from decreased stopping and increased zirconium fraction in the film caused by loss of hydrogen, carbon, and excess oxygen. For similar reasons the silicon edge (channel 420) moves to higher energy with dose, and the oxygen peak becomes narrower (channel 310). The oxygen peak should also decrease in height as well as width with dose, but the relative insensitivity of the RBS technique to light atomic species makes observation difficult. A trace amount of hafnium is present due to impurities in the ceramic precursor. Figure 1b indicates the loss of hydrogen with increasing dose commiserate with the indirect evidence of species loss in figure 1a. A similar decrease of the carbon peak is observed for the RBS spectra taken at a beam energy of 3.6 MeV (not shown). These observations are consistent with our previous investigation of implantation of xenon ions into sol-gel zirconia films[3,4].

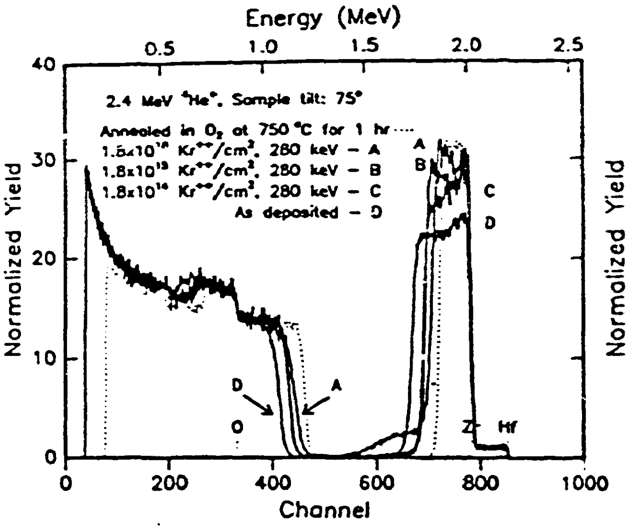

Figure 1a. RBS spectra of Kr implanted sol-gel zirconia on Si substrates. Surface markers are given for Zr, Hf, and O.

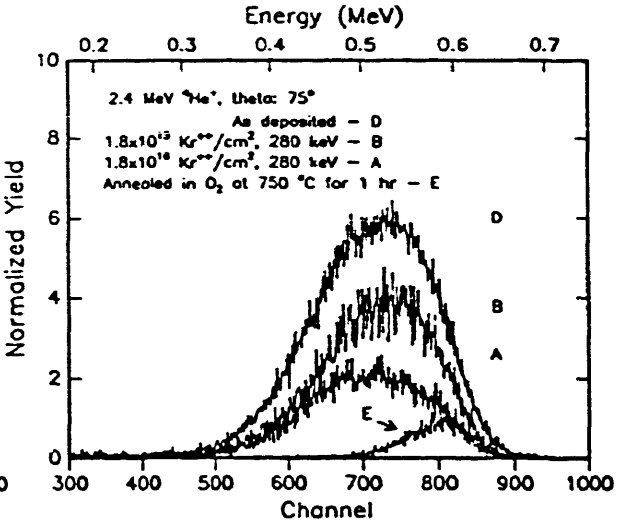

Figure 1b. Hydrogen FRES spectra of Kr implanted sol-gel zirconia on Si substrates

Also shown for comparison in figures 1a and 1b are the RBS and FRES spectra for the as-deposited and annealed samples. The FRES spectrum of the conventionally annealed sample contains a small peak which is shifted to higher energy relative to the other spectra. This peak is characteristic of adsorbed water onto the sample surface. Although the height of the zirconium peak of the highest dose implant in figure 1a approaches that of the conventionally annealed sample, Figure 1b indicates that a substantial amount of hydrogen still remains in the film.

Figure 2 below shows the densification fraction of hydrogen evolved for all samples as a function of electronic energy loss. Although it was originally thought that densification might be a strong function of nuclear energy deposition, our results indicate that the densification is more strongly dependent on electronic energy loss as is evidenced by figure 2, in which a curve has been drawn to guide the eye.

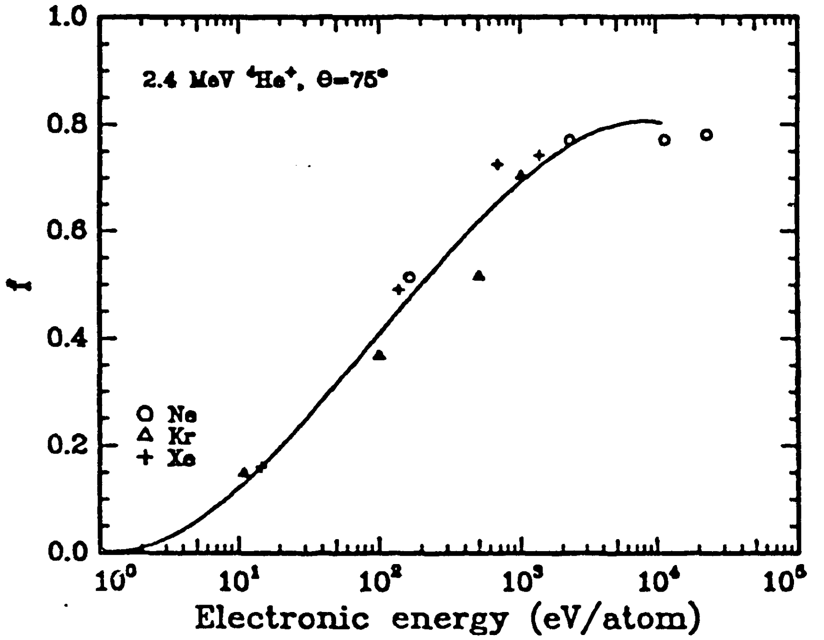

Figure 2 Densification fraction of hydrogen evolved as a function of electronic energy deposited. The curve serves to guide the eye.

Figure 3 show the densification fraction as characterized by the carbon content measured at a beam energy of 3.6 MeV for the krypton and xenon implants. As a trend is not as readily discernible, carbon content measurements are not as useful in discriminating between nuclear and electronic energy loss dependence of densificaton. This results from the relatively small amount of carbon initially present in the films and the corresponding statistical error involved in the measurement thereof.

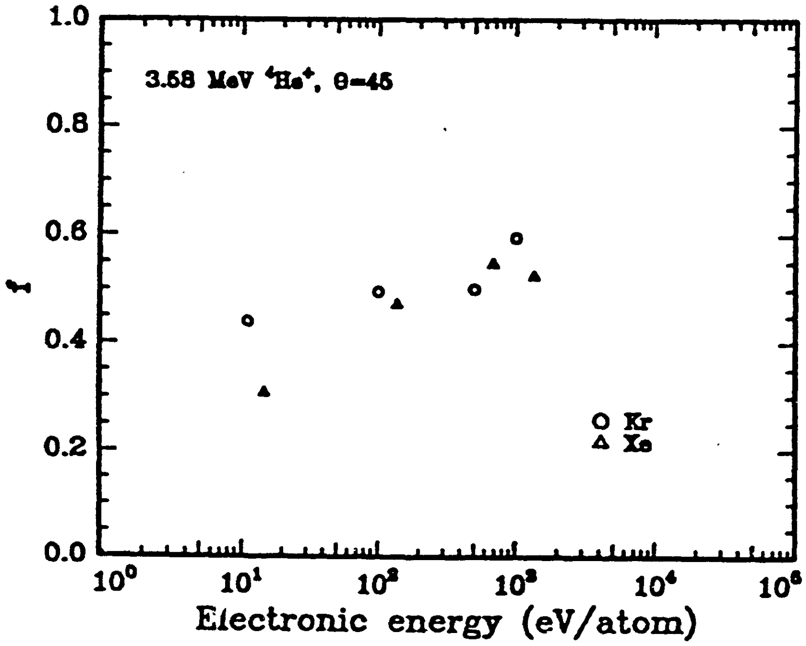

Figure 3. Densification fraction of carbon evolved as a function of electronic energy deposition

Since electronic energy deposition seems to be the more relevant energy transfer mode than nuclear energy deposition to the observed densificaton, it may be worthwhile to consider the work done on ion irradiation of polymers as reviewed by Venkatesan[8]. The behavior of polymers under ion irradiation has been shown to depend on the ion, the ion energy and the chemstry of the target. But many polymers display similar effects such as cross linking, chain scission, and evolution of volatile species resulting from ionization of target atoms and bond cleavage. The observed phenomena correlate with total energy deposition. At the high ion energy regime studied (typically > 1MeV) most of the ion energy is dissipated in electronic energy loss modes. Calcagno et. al. attributed an abrupt change in the solubility of polystyrene under ion irradiation to the formation of carbon chains into a three dimensional carbon network [9]. It is supposed that each one of these plays a role in the ion-beam-induced densification of sol-gel zirconia thin films.

CONCLUSION & FUTURE DIRECTIONS

We have observed densification of sol-gel derived zirconia thin films via irradiation of various inert gas ions. The observed densification, as characterized primarily by changes in hydrogen content, correlates strongly with electronic energy deposition. This result along with the knowledge of the polymeric nature of the inorganic ceramic precursor suggests that ion-beam-induced densification is similar to ion irradiation of organic polymers for which target ionization induces cross linking and chain scission with a commiserate liberation of volatile species.

To more fully explore this behavior, it is worthwhile to perform a similar study where equivalent amounts of electronic energy through ion irradiation are deposited in the films. In addition, use of electron beams to irradiate sol-gel zirconia thin films may further the understanding of ion-beam-induced densification.

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