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Effects of nuclear and electronic stopping powers on the conversion of hybrid silicate thin films

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ABSTRACT

A study of the effects of nuclear and electronic stopping powers on the ion irradiation-induced conversion of hybrid silicate thin films is presented. The films were synthesized by sol-gel processing from a combination of tetraethylorthosilicate (TEOS) and methyltriethoxysilane (MTES) precursors and were spin-coated onto a Si substrate. After drying at 300 °C for 10 min, the films were irradiated with either 400 keV N^{2+} or 1 MeV Cu^{+} at fluences ranging from 1×10^{13} to 1×10^{16} ions/cm^2. The ion species and energies were chosen such that electronic stopping powers were similar while nuclear stopping powers varied. The electronic and nuclear stopping powers of the ions in the films were calculated as a function of depth. The effects of stopping power on the film conversion were studied in terms of film shrinkage and nanomechanical response by utilizing atomic force microscopy and nanoindentation. Ion irradiation at lower fluences had a negligible effect on the hardness and reduced elastic modulus. However, after ion irradiation with a fluence of 1×10^{15} ions/cm^2, the film irradiated with 1 MeV Cu^{+} had higher hardness and elastic modulus compared to the film irradiated with 400 keV N^{2+}, suggesting the mechanical properties of the resulting thin films were related to both the electronic and nuclear stopping powers. After ion irradiation with a fluence of 1×10^{16} ions/cm^2, the difference in the hardness and elastic modulus of the two irradiated films became smaller.

1. Introduction

Sol-gel derived Si-based materials have been used in many different applications including metal corrosion inhibitors [1–3], abrasion resistant coatings [4,5], micro-components in MEMS [6,7], and electrochemical biosensors [8,9]. Our previous studies have also demonstrated their suitability in fabricating diamond-machinable optical molds for high volume and low-cost production of microstructured complex optics [10,11].

In the conversion of sol-gel derived polymers to their ceramic state, ion irradiation has been of great interest as an alternative to heat treatment [12–18]. Modification of the organic/inorganic films by ion irradiation leads to substantial changes in the resulting mechanical properties, chemical composition, and microstructure. Radiation of various types of polysiloxanes, a general term for organic polymers containing a –Si–O–Si– backbone, with He, C and Au ions at maximum achievable fluences resulted in the formation of hard ceramic coatings with hardnesses ranging from 15 GPa to 21 GPa [13,19]. Ion irradiation leads to chemical changes in the polymer chain, namely, chain scission and crosslinking, along with the formation of dangling bonds and the release of volatile gas molecules [20–23]. The microstructural evolution as a result of ion irradiation with different irradiating parameters, such as ion species, incident energies, and fluences, has been studied in our previous work [24,25]. Previous research efforts on the relative contribution of electronic and nuclear stopping power in the polymer-ceramic conversion process, however, are limited. In this work, we present a study on the roles of electronic and nuclear stopping power in the conversion of sol-gel films, derived from tetraethylorthosilicate (TEOS) and methyltriethoxysilane (MTES) precursors, to ceramics. Film shrinkage and the changes in mechanical properties are investigated.

2. Materials and methods

Silica-based sol-gel films were synthesized by sol-gel processing. Starting with a solution of 7.5 mol ethanol, 1 mol distilled water, and 1 mol acetic acid in a beaker, a mixture of 0.4 mol tetraethoxysilane

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(TEOS, $Si(OC_2H_5)_4$) and 0.6 mol methyltriethoxysilane (MTES, $CH_3Si(OC_2H_5)_3$) was added drop by drop to the solution under vigorous stirring. The resulting solution was stirred for 10 min before adding 0.25 mol PVP ($(C_6H_9NO)_n$), after which the solution was sealed and heated above 50 °C for 30 min. After cooling, the sol was stored in a glass bottle in an Ar atmosphere for 24 h. Then the sol was deposited by spin coating onto polished 50 mm diameter (1 0 0) Si wafers. The films were allowed to dry at 80 °C for at least 10 min, then heat treated in a pre-heated furnace at a temperature of 300 °C for 10 min. The resulting films had thicknesses of ~1 μm, as determined by step height measurements using AFM. The film density was estimated to be ~1.0 g/cm^3 based on the measured film thickness, the coated area of the film, and the measured weight gain of the Si wafer after deposition and heat treatment. Individual specimens approximately 25 mm × 25 mm in size were cleaved for subsequent ion irradiations.

The films on the cleaved specimens were irradiated with either 400 keV N^{2+} or 1 MeV Cu^+ at a fluence between 1×10^{13} and 1×10^{16} ions/cm^2. The ion species and incident energies were chosen such that (a) the incident ions had similar averaged electronic stopping power, but significantly different nuclear stopping power, to enable the comparison of the roles of electronic and nuclear stopping in the conversion process; (b) the projected ranges of all the incident ions was greater than the film thickness to achieve a full irradiation through the film thickness and to minimize the effects of chemical bonding between the incident ions and the target atoms and on any resulting changes in the mechanical and chemical properties. During ion irradiation, the beam current was limited at 0.5 μA/cm^2 to avoid the accumulation of significant heat.

The electronic and nuclear stopping powers were obtained through Monte-Carlo simulations using SRIM [26]. Fig. 1 shows the depth distribution of electronic and nuclear stopping power of 400 keV N^{2+} and 1 MeV Cu^+ in the sol-gel film and Si substrate. The energy loss of 400 keV N^{2+} in the sol-gel film is dominated by electronic stopping. The electronic and nuclear stopping contribute equally to the energy loss of 1 MeV Cu^+ in the sol-gel film. The averaged electronic stopping over the film thickness for 400 keV N^{2+} and 1 MeV Cu^+ are approximately the same. Table 1 shows the averaged electronic and nuclear stopping power of 400 keV N^{2+} and 1 MeV Cu^+ over the film thickness, as well as the total stopping power (the sum of the electronic and nuclear stopping power). The projected ranges of the ions are also shown. Considering the longitudinal straggling, ~120 nm for 400 keV N^{2+} and ~180 nm for 1 MeV Cu^+, almost all the incident ions eventually rest in the substrate.

Film shrinkage was determined by measuring the film thickness before and after ion irradiation using AFM. The changes in the mechanical properties (hardness and reduced elastic modulus) of the film as a result of ion irradiation were investigated by performing load-controlled nanoindentation with a Berkovich diamond indenter.

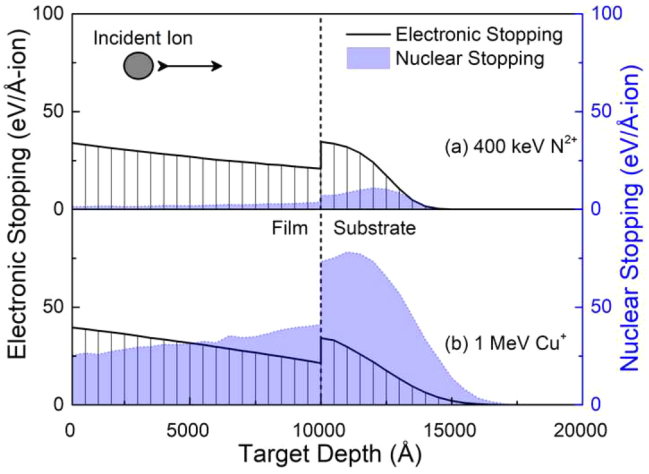

Fig. 1. Electronic and nuclear stopping power of (a) 400 keV N^{2+} and (b) 1 MeV Cu^+ in sol-gel films on Si substrates.

Table 1
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Ion irradiation	400 keV N^{2+}	1 MeV Cu^+
Electronic stopping power (eV/Å-ion)	27.9	30.9
Nuclear stopping power (eV/Å-ion)	2.2	32.6
Total stopping power (eV/Å-ion)	29.1	63.5
Projected range (μm)	1.24	1.26

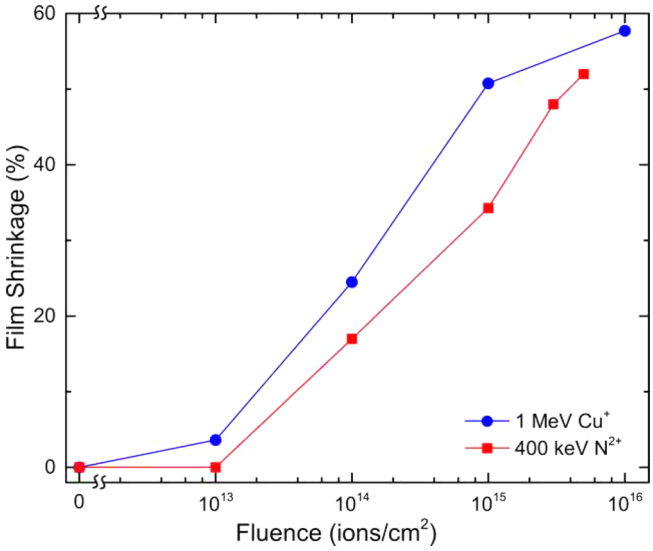

Fig. 2. Shrinkage of the sol-gel films irradiated with 400 keV N^{2+} and 1 MeV Cu^+ as a function of fluence.

3. Results and discussion

Ion irradiation of the sol-gel films resulted in film shrinkage. Fig. 2 shows shrinkage of the films irradiated with 400 keV N^{2+} and 1 MeV Cu^+ at varying fluences. Film shrinkage increased monotonically with increasing fluence, which is consistent with the continuous decomposition of the organic materials, as was observed previously by FT-IR [24,25]. Less than 5% film shrinkage was measured for the films irradiated with either ion at a fluence of 10^{13} ions/cm^2. Irradiation with 400 keV N^{2+} and 1 MeV Cu^+ introduced a film shrinkage of 17% and 24% at a fluence of 10^{14} ions/cm^2, and 34% and 51% at a fluence of 10^{15} ions/cm^2, respectively. In general, within the range of fluences used, 1 MeV Cu^+ which had similar electronic stopping but higher nuclear stopping than 400 keV N^{2+} introduced greater shrinkage for a given fluence.

Hardness and reduced elastic modulus of the irradiated films were measured using nanoindentation. Before performing nanoindentation the surface roughness of the unirradiated and irradiated films was found to be ~1 nm rms over a scan size of 1 μm^2 as measured by AFM. There was no clear indentation size effect observed on all the films investigated over a range of contact depths from 30 to 200 nm. The near surface hardness and reduced elastic modulus, evaluated at a contact depth of 30 nm for all irradiated films as a function of fluence, are shown in Fig. 3. Also shown is an unirradiated film having near surface hardness of 0.3 GPa and reduced elastic modulus of 6.4 GPa. All reported data are the average of five indentations with the error bars representing the maximum and minimum values measured. Ion irradiation at a fluence of 10^{13} ions/cm^2 led to a negligible change in the measured hardness and reduced elastic modulus for either ion species.

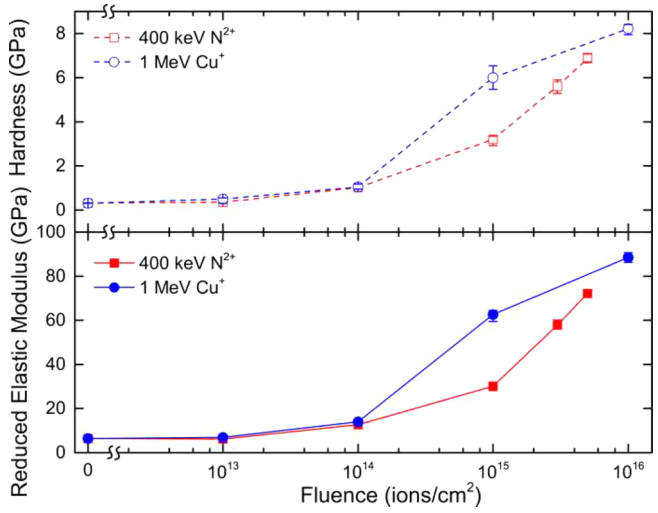

Fig. 3. Near surface hardness and reduced elastic modulus evaluated at a contact depth of 30 nm for 400 keV N^{2+} and 1 MeV Cu^{+} irradiated sol-gel films as a function of fluence.

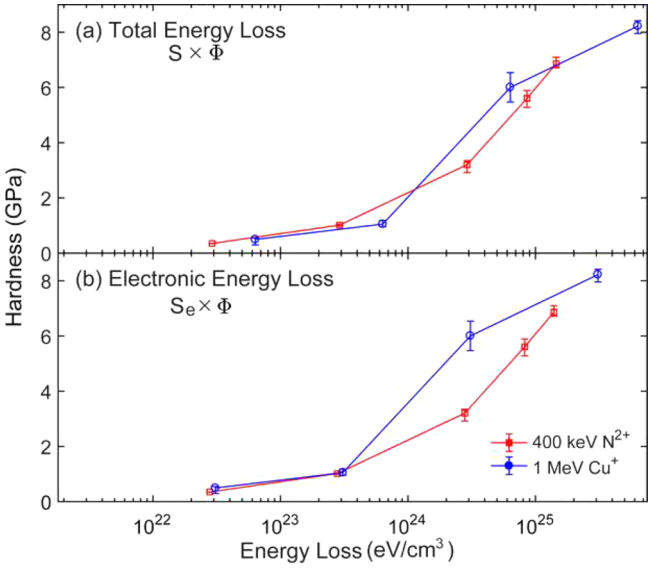

Fig. 4. Near surface hardness evaluated at a contact depth of 30 nm for 400 keV N^{2+} and 1 MeV Cu^{+} irradiated sol-gel films as a function of total energy loss and electronic energy loss.

After irradiation at a fluence of 10^{14} ions/cm^2, there was a slight increase in the hardness and reduced elastic modulus over that of the unirradiated film. At this fluence both 400 keV N^{2+} and 1 MeV Cu^{+} irradiation resulted in nearly the same measured mechanical properties with a near surface hardness of 1.0 GPa and reduced elastic modulus of 13.3 GPa. When irradiated at a fluence of 10^{15} ions/cm^2, the film irradiated with 1 MeV Cu^{+} exhibited a higher film shrinkage and double the hardness and reduced elastic modulus of that irradiated with 400 keV N^{2+}. This indicates at a fluence of 10^{15} ions/cm^2 there is a considerable contribution from nuclear stopping to the polymer-ceramic conversion process as reflected in changes in film shrinkage, hardness, and reduced elastic modulus, which was not evident at lower fluences. For irradiation with either ion at even higher fluences, both the hardness and reduced elastic modulus increased further with increasing fluence within the investigated range of fluences. However, the difference in the measured hardness of the films irradiated with 400 keV N^{2+} and 1 MeV Cu^{+} at the same fluence gradually decreased with increasing fluence. This also applies to the difference in the measured reduced elastic modulus. Although irradiation with 1 MeV Cu^{+} was not performed at an intermediate fluence between 10^{15} and 10^{16} ions/cm^2, the Cu^{+} irradiated films are expected to have higher hardness and reduced elastic modulus than the N^{2+} irradiated films at the same fluence. This is supported by the observation that with increasing fluence, the hardness and reduced elastic modulus increased and the rate of increase gradually decreased at higher fluences.

When irradiated at a fluence of 10^{15} ions/cm^2, there is a significant increase in the hardness and reduced elastic modulus over that of the unirradiated film. The film irradiated with 400 keV N^{2+} exhibited a near surface hardness of 3.2 GPa and reduced elastic modulus of 30.1 GPa, and the film irradiated with 1 MeV Cu^{+} had a near surface hardness of 6.0 GPa and reduced elastic modulus of 62.6 GPa. This could be attributed to, in part, the changes in the silica structure and the formation of a three-dimensional interconnected SiOC structure, where silicon is simultaneously bonded with carbon and oxygen in the amorphous network [27–34]. The presence of the SiOC structure has been confirmed by the appearance of an O-Si-C peak in the FT-IR spectra in our previous studies [24,25]. The hardness of the film irradiated with 1 MeV Cu^{+} at the maximum fluence (8.2 GPa) is about 7-times higher than a film converted by pyrolysis at 800 °C for 30 min in vacuum, while the reduced elastic modulus (88.6 GPa) is more than 5-times higher than after the heat treatment [35].

The near surface hardness of the irradiated films showed a non-linear increase with increasing fluence for each ion species as shown in Fig. 3. The effects of energy loss on the near surface hardness of the irradiated films are shown in Fig. 4 by plotting the near surface hardness as a function of (a) total energy loss per unit volume S× Φ, (b) electronic energy loss per unit volume $S_e \times \Phi$, where S_e and Srepresent the electronic and the sum of electronic and nuclear stopping power, and Φ is the fluence. As previously discussed, the effects of ion irradiation on the mechanical properties at lower fluences (below 10^{15} ions/cm^2) were small and the contribution of nuclear stopping to the change in hardness and reduced elastic modulus was not measurable. At higher fluences, when the electronic energy loss is greater than $\sim 3.0 \times 10^{23}$ eV/cm^3, the films irradiated with 1 MeV Cu^{+} exhibited a different hardening behavior as a function of electronic energy loss compared to those irradiated with 400 keV N^{2+}. As shown in Fig. 4(b) at a given electronic energy loss above $\sim 3.0 \times 10^{23}$ eV/cm^3, the film irradiated with 1 MeV Cu^{+} had a higher hardness than that irradiated with 400 keV N^{2+}. The resulting hardness of the irradiated films followed a single relationship with the total energy deposited irrespective of the irradiating ion species as shown in Fig. 4(a). It is well recognized that electronic stopping is of significant importance in the enhancement of the surface mechanical properties of irradiated polymers, whereas the effect of nuclear stopping is still controversial [21,22,36,37]. Our results suggest that nuclear stopping contributes to the hardening mechanism of the irradiated sol-gel films.

4. Conclusions

Film shrinkage, hardness and reduced elastic modulus of sol-gel derived Si-based films, subjected to irradiation with two different ions that have similar electronic stopping but significantly different nuclear stopping, were studied. The importance of electronic stopping in the polymer-ceramic conversion process and the resulting increase in hardness and elastic modulus is well recognized. The effects of nuclear stopping on these conversion processes, however, is still controversial. In our study, films irradiated with ions having higher nuclear stopping (or total stopping), exhibited a greater shrinkage, near surface hardness, and reduced elastic modulus at a given fluence. Therefore it is seen that nuclear stopping contributes to the hardening mechanism of the irradiated films.

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