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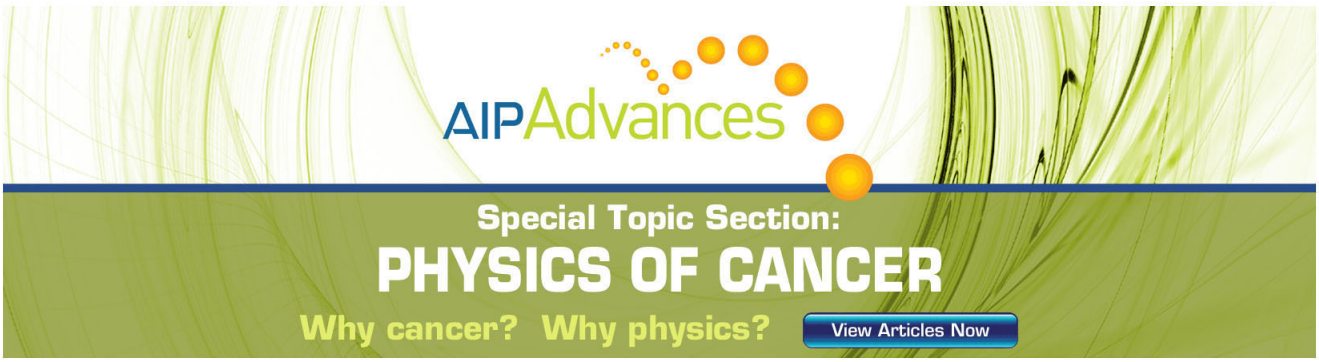

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Low-damage milling of an amino acid thin film with cluster ion beam

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In this work, we characterized the surface damage layer and sputtering yield of polycrystalline L-leucine films before and after irradiation with Ar cluster or monomer ion beams with x ray photoelectron spectroscopy and ellipsometry. Irradiation with Ar monomer ion beams induced heavy damage on the surface of L-leucine films, such as bond breaking and carbonization. In contrast, no significant surface damage was observed in the films irradiated with Ar cluster ion beams. The sputtering yield of L-leucine decreased dramatically with increasing fluence of monomer Ar ions and approached the value of the sputtering yield of graphite; but under irradiation with Ar cluster ion beams, the sputtering yield remained constant with fluence. The differences in sputtering yield behavior were explained in relation with the surface damage layer on organic materials. Thus, cluster ion beams could potentially be used to mill down biological materials without significant damage on the surface and could contribute to various applications in the analysis and processing of life matter. © *2011 American Institute of Physics*. [doi:10.1063/1.3658220]

I. INTRODUCTION

Because of its potential in the fields of nanoscaled fabrication[1–3] and mass analysis of organic and biological materials,[4,5] ion beam technology has attracted much interest in the research community. Chemical etching and methods of direct slicing, i.e., microtome, have been applied in the fabrication of organic devices and analysis of the surface or the bulk of organic and life matter. The need for ion beam etching (milling) of organic materials without damage to the structure has been identified for fabrication and analysis. Irradiation with a conventional ion beam induces heavy damage on the surface of organic materials, including effects such as chemical bond breaking, recombination, and carbonization.[6,7] The carbonization occurs in irradiation with ion beams because of the "selective sputtering" effect, which refers to the fact that oxygen, hydrogen, and nitrogen are sputtered from the sample surface at a higher yield than carbon. The carbonized layer thickness accumulates to eventually reach the projection range of the ion beam. Carbonization often reduces the sputtering (milling) rate of the organic materials, resulting in an inhomogeneous surface.

Gas cluster ion beams consist of several hundred to several thousand atoms or molecules, and, as reported, its irradiation effects on organic or polymeric materials are completely different from those of a monomer ion beam, with high sputtering yield and low damage.[5,8–11]

L-leucine ($C_6H_{13}NO_2$, 131 u) is one of the essential amino acids and is a common substance in living cells. It consists of fundamental elements of biological materials, namely carbon, hydrogen, nitrogen, and oxygen, and therefore was considered to be very appropriate to investigate the ion beam irradiation effect on organic materials. The damage on the L-leucine films irradiated with high fluence ($\sim 10^{15}$ ions/cm^2) of Ar cluster or monomer ion beams has been investigated with scanning electron microscope, secondary ion mass spectrometry, and ellipsometry. The surface of the L-leucine completely changed to carbon structure with irradiation of an Ar monomer ion beam. In contrast, changes were not observed on the surface of the L-leucine film irradiated with Ar cluster ion beams. In this study, we used x-ray photoelectron spectroscopy (XPS) and ellipsometry to evaluate the surface damage layer and sputtering yield of polycrystalline L-leucine film after irradiation with a large Ar gas cluster or conventional monomer Ar ion beam. We focused on the chemical bond breaking of L-leucine with irradiation of relatively low fluence ($\sim 10^{13}$ ions/cm^2) of Ar cluster or monomer ion beams. XPS enables sensitive measurements of the chemical bonds on the sample surface (5–10 nm), and ellipsometry can determine film thickness of very soft organic materials. These procedures could be adopted for characterization of ion-beam damaged surface layers in organic materials.

II. EXPERIMENTAL PROCEDURE

The L-leucine films were deposited on crystalline silicon (c-Si) substrates. The substrate wafers were cleaned of any residual organic materials in a cleaning cycle using water, acetone, trichloroethylene, acetone, and water again, 10 min for each fluid, in an ultrasonic bath. After cleaning, the wafers were dried with nitrogen gas. L-leucine was deposited in a vacuum chamber (evacuated to 4×10^{-5} Pa with a cryogenic pump) by thermal evaporation using a tantalum boat. The deposition rate was 0.4–0.6 nm/s, the film was 120 nm thick, and its density was ~ 0.80 g/cm^3 ($\sim$70%), obtained

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using a 20-nm-thick L-leucine film with x ray reflective (XRR) measurements (see Fig. 1 for a typical spectrum).[12,13] The L-leucine films were characterized as polycrystalline using x ray diffraction (XRD) with Cu Kα x ray radiation and a computer-controlled reflectometer (Rigaku, ATX-G, 18 kW). The mean grain size was calculated as ~40 nm based on the full-width-half-maximum (FWHM) of the XRD line of the L-leucine (100) plane[14,15] and the Scherrer equation (Fig. 2).[16,17] Surface roughness was measured with atomic force microscopy (AFM) (Shimadzu, SPM9500J2) and the AFM tomography image was taken in the tapping mode. The average surface roughness (Ra) was ~4 nm on a scanning area of 10 μm × 10 μm (Fig. 3). The deposited film with surface roughness of ~4 nm consisted of 70% polycrystalline L-leucine with a mean grain size of ~40 nm and 30% vacancies.

To generate the Ar gas cluster ion beam, we used the adiabatic expansion of a high-pressure argon through a nozzle. The neutral clusters were ionized by electron bombardment at a voltage of 300 V and a current of 50 mA and were electrostatically accelerated in this work to 10 or 20 keV. Monomer ions were removed from ion beam with strong magnetic fields. The source gas pressure was 5.3×10^5 Pa, and the mean size of the Ar cluster ion beam was 5000, as measured using the time-of fight method. The irradiation fluence of the Ar cluster ion beams was 2.0×10^{13}–2.5×10^{14} ions/cm^2. To compare between irradiation effects of cluster and monomer ion beams, the L-leucine films were also irradiated with Ar monomer ion beams accelerated to 10 keV, and the properties were characterized with the same procedure. The ion fluence of the Ar monomer ion beams was also 2.0×10^{13}–5.0×10^{14} ions/cm^2.

The surface of the L-leucine films was characterized with XPS with Al Kα x ray radiation (ULVAC-PHI Quantum-2000). Irradiation with an Ar cluster ion beam was performed at the acceleration voltage of 10 keV and 20 keV and with the Ar monomer ion beam at the acceleration voltage of 10 keV. The ion fluence was 2.0×10^{13} ions/cm^2. The x ray beam spot was 20 μm in diameter, and the take-off angle of the photoelectron was 45°. XPS spectra were taken in the narrow condition, i.e., near the range of C 1s (276–296 eV),

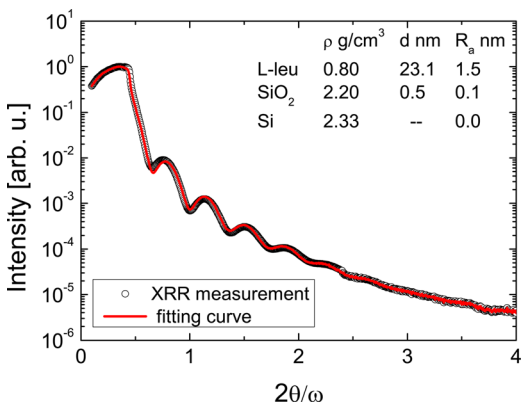

FIG. 1. (Color online) XRR spectrum obtained from the L-leucine. The fitting curve was calculated in the multilayer model of the XRR software with the shown fitting parameters (density (ρ), thickness (d), and surface roughness (R_a)).

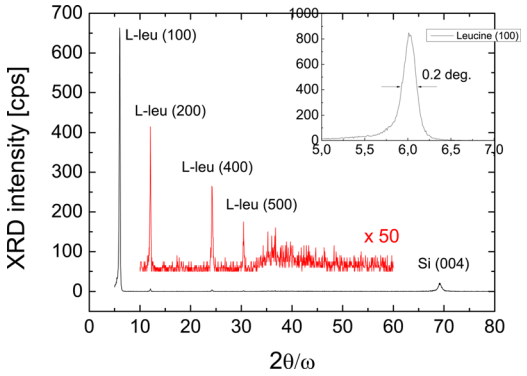

FIG. 2. (Color online) XRD spectrum of the L-leucine film showing diffraction lines from the (100) plane and multi-order lines of the same plane. The FWHM of (100) line was 0.2° (inset).

N 1s (392–412 eV), and O 1s (525–545 eV). The probing depth of XPS was 5–10 nm, as determined by the escaping depth of an emitted photoelectron from the sample. The thickness of the L-leucine film was also measured using conventional single-wavelength (635 nm) ellipsometry before and after irradiation with an Ar cluster or monomer ion beams. The incident angle of the laser was 75°. The refractive index of L-leucine film of 70% density was calculated as 1.37 with an effective medium approximation model.[13,18,19]

III. RESULTS AND DISCUSSION

Changes in the chemical bonds of L-leucine at the probing depth of 5–10 nm were observed with XPS. The sputtered film depth (10–20 nm) was larger than the surface roughness value (~4 nm), but shorter than the mean grain size of the L-leucine crystal (~40 nm); therefore, an accurate analysis could be operated with this probing depth. The XPS spectra near the range of C 1s, N 1s, and O 1s, respectively, are shown in Figs. 4(a)–4(c). The core level electrons ejected from each atom, which is influenced by bonding environments, and small chemical shift indicates the bonding environments. In the spectrum near the range of C 1s from the as-received (unirradiated) film (Fig. 4(a)), the peak at ~285 eV corresponds to C–C, C–H (284.8 eV), and C–N

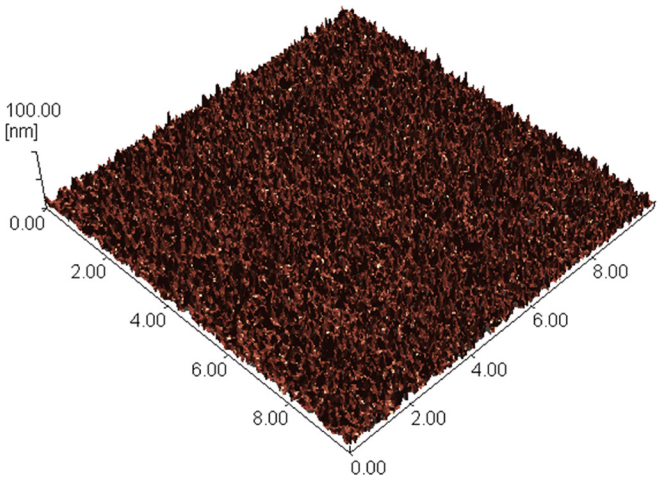

FIG. 3. (Color online) AFM tomography image on the surface of the L-leucine film.

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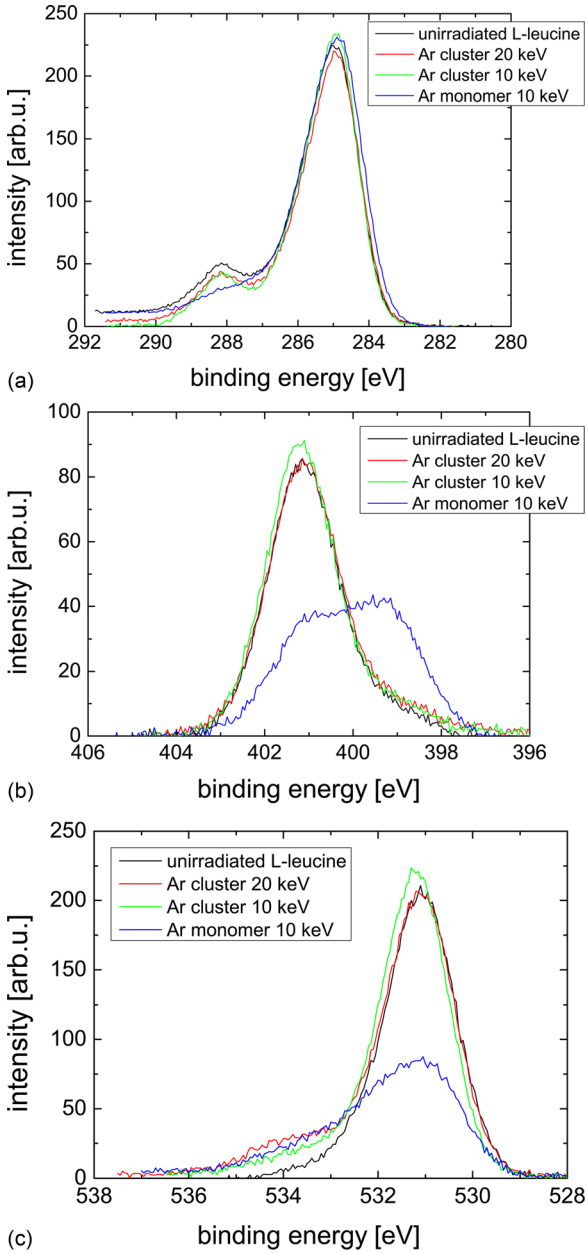

FIG. 4. (Color online) XPS spectra from the L-leucine films before and after irradiation with Ar cluster or monomer ion beams near the range of C 1s (a), N 1s (b), and O 1s (c). (For the color codes, see insets).

(285.9 eV) bonds, and that at ~288 eV consisted of O=C–O (288.1 eV) bonds. The spectra from the L-leucine films irradiated with an Ar cluster ion beam at the energy of 10 and 20 keV were almost similar with those from the unirradiated L-leucine film, but the peak corresponding to O=C–O bonds had a slight (less than 10%) loss in intensity. In contrast, for the L-leucine film irradiated with an Ar monomer ion beam, the peak corresponding to O=C–O had an intensity loss of ~40%. These results suggested that only few O=C–O bonds were broken by irradiation with the Ar cluster ion, but irradiation with the monomer ion beam caused a larger proportion of these bonds to break. The two peaks in Fig. 4(b), the big one at ~401 eV and a smaller one at ~399 eV, correspond to C–N bonds. L-leucine is stabilized as zwitterion in neutral pH (Fig. 5).[20] The electron-escaping energy from the

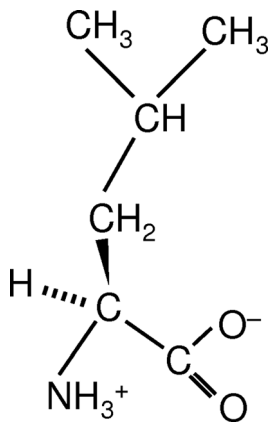

FIG. 5. The structure of L-leucine in zwitterion form.

N atom affected by the C–NH_2 bond is 399.2 eV, and that by the C–NH_3^+ bond is 401.2 eV.[21] In the unirradiated film, almost all the L-leucine molecules formed as zwitterion, and it did not change with Ar cluster ion irradiation. In contrast, ~50% of the C–NH_3^+ bonds became C–NH_2 with Ar monomer ion beam irradiation, and the integrated intensity of the C–N bonds also decreased by ~10% after the irradiation with the Ar monomer ion beam. This indicated that the zwitterion structure of L-leucine still remained almost intact after it was irradiated with Ar cluster ion beam irradiation, but could not withstand irradiation with the Ar monomer ion beam. In Fig. 4(c), the peak at the energy of 531.0 eV corresponds to the electron escaped from the O atom affected by O=C–O^- bonds. The electron-escaping energy of the O atom affected by C–OH and O=C is 532.0 and 533.7 eV, respectively, and almost all of the L-leucine molecules formed as zwitterion in the as-received film (Fig. 4(c)). After irradiation with Ar cluster ion beams, the peaks were slightly shifted from O=C–O^- bonds to O=C–OH bonds. Irradiation with the Ar monomer ion beam caused a significant decrease in peak intensity of the O=C–O^- bonds, and peak position has also shifted from O=C–O^- bonds to O=C–OH bonds. This decrease in intensity is attributed to the selective sputtering effect, as O atoms were easily sputtered compared with C or N atoms. The stoichiometry of the various L-leucine films before and after irradiation with the Ar cluster (10 and 20 keV) or monomer ion beams is shown in Fig. 6. The C atom fraction in the unirradiated film was ~70%, and in the film irradiated with the Ar monomer, it increased to ~80%. However, no significant damage was observed on the surface of the films irradiated with the Ar cluster ion beams. Overall, the XPS results suggested that irradiation of L-leucine films with the Ar monomer ion beam induced heavy damage, which included bond breaking, structural change, and carbonization on the film surface; whereas the Ar cluster ion beam induced little bond breaking or structural change on the surface.

The sputtered film depth increased linearly with irradiation fluence under irradiation with the Ar cluster ion beam (10 and 20 keV) (Fig. 7). Under irradiation with the Ar monomer ion, the sputtered depth increased linearly up to a fluence value below 10^{14} ions/cm^2, and the slope of the sputtered film depth decreased at a fluence value over 10^{14}

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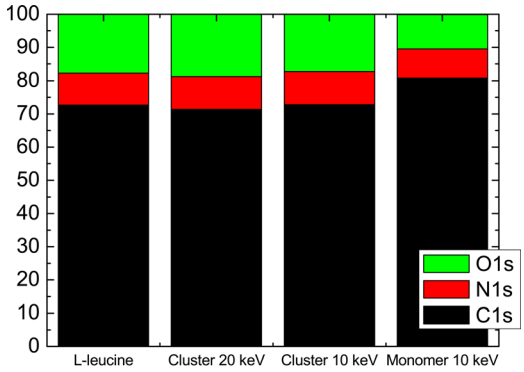

FIG. 6. (Color online) The elemental ratios of L-leucine before and after irradiation with Ar cluster or monomer ion beams.

ions/cm^2. The sputtering yield, which is defined as the number of sputtered molecules per incident ion, can be calculated using the incident ion fluence, sputtered film depth, density, and molecular weight. The sputtering yield of the L-leucine was 410 ± 5 and 170 ± 5 molecules with irradiation of one incident cluster ion with energy of 20 and 10 keV, respectively, which agreed well with previously reported sputtering yields measured with a contact profiler or ellipsometry.[22,23] These values were constant over the irradiation fluence range of 10^{14}–10^{15} ions/cm^2. With irradiation of the Ar monomer ion, the sputtering yield of L-leucine was 240 ± 10 molecules in the linear region (10^{13}–10^{14} ions/cm^2), decreasing to 3 ± 1 molecules in the saturated region (10^{14}–10^{15} ions/cm^2). With Ar monomer ion irradiation, the sputtering yield of L-leucine in the linear region was similar to that with the Ar cluster, and it approached the sputtering yield of graphite irradiated with the Ar monomer ion (calculated to be 1.1 by a semiempirical formula).[24] The sputtered volume of L-leucine with irradiation of the Ar cluster at the energy of 10 and 20 keV and with the Ar monomer at the energy of 10 keV was 44, 110, and 64 nm^3, respectively, and the sputtered film depth was estimated as approximately 3–5 nm. The sputtering mechanism with cluster ion beams has been explained with the multiple collision effect, which refers to thousands of low energy ions colliding on the sample simultaneously and causing the surface material to be sputtered.

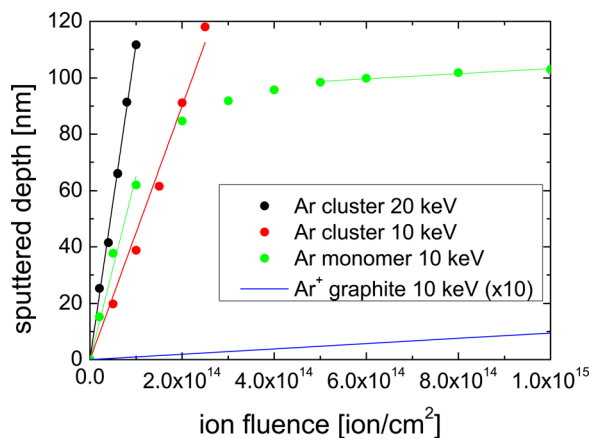

FIG. 7. (Color online) Sputtered depth with Ar cluster or monomer ion irradiation as a function of fluence (for color codes, see inset).

Not every atom in the cluster can penetrate the sample, and the beam projection range would be quite thin (~1 nm); therefore, the surface damage layer would be removed by sputtering and a damage layer that is quite thin would be localized on the surface. On the other hand, the projection range of the Ar monomer ion beam in L-leucine is 30 nm and is much deeper than the sputtered film depth.[25] Thus, the surface damage layer (carbonized layer) cannot be removed by sputtering, and damage would accumulate deep in the sample. This tendency of carbonization by irradiation with the Ar monomer ion beam was consistent with the results of XPS measurements.

IV. CONCLUSIONS

L-leucine polycrystalline films were characterized before and after irradiation with Ar cluster or monomer ion beams using XPS, which applied to estimate the surface damage on the surface of the L-leucine films, and ellipsometry, which was used mainly to measure sputtering yields. Irradiation with irradiation of an Ar monomer ion beam induced heavy damage, such as bond breaking, structural change, and carbonization on the surface of L-leucine films. The C atom fraction in the unirradiated film was ~70% and, in the film irradiated with Ar monomer, it increased to ~80%. However, no significant damage was observed on the surface of the films irradiated with Ar cluster ion beams. Irradiation with Ar monomer ion beams at a fluence of 10^{14} ions/cm^2 reduced the L-leucine sputtering yield dramatically, with values approaching the sputtering yield of graphite. This was attributed to accumulation of carbonization damage on the surface of L-leucine films. In contrast, the sputtering yield after irradiation with Ar cluster ion beams was constant with fluence, and all the films were removed with irradiation. These results were consistent with the results obtained by XPS. This study proved that cluster ion beams have the potential to slice down amino acids without significant damage on the surface. As a further application, it is interesting to note that this technique could contribute to various applications in the analysis and fabrication of biological materials.

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