Notes

Laser Ablation of Poly(methyl methacrylate) at 266 nm

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Polymer films have been deposited by diverse techniques such as vacuum evaporation, plasma polymerization, electrochemical polymerization, and spin coating.[1] Recently, deposition of polymer films by UV laser ablation was proved to be a promising technology for the preparation of hardly processible polymer materials.[2] Since the pioneering work by Srinivasan *et al.*,[3] laser ablation of polymer materials has been the object of growing interest due to potential applications in electronic technology and the lure of discovering their fundamental properties.

In general, two typical mechanisms of material ejection by UV laser ablation of polymers are thought to exist: photochemical[4] and photothermal.[5] Bond-breaking and material ejection are believed to occur directly from the excited electronic state in the photochemical mechanism. Alternatively, in the photothermal mechanism, the electronic energy is converted to heat *via* radiationless transitions followed by thermal "unzipping" of the polymer.[6] Also, a phenomenon called incubation has been reported often for certain polymer materials.[7,8] Incubation occurs when a weakly absorbing polymer material is converted to a material with a higher absorption cross section after repetitive exposure through photochemical and/or photothermal reactions.[8]

Here, we report preliminary experimental results on the ablation mechanisms of poly(methyl methacrylate) (PMMA) at 266 nm by analyzing both neutral and cationic products using quadrupole mass spectrometry. Among many polymeric materials, PMMA has been the most intensively examined target material to elucidate ablation mechanisms. In addition to the ablation study, we have attempted to fabricate PMMA and PMMA/Cu bilayer films on Si substrate by pulsed laser deposition. This will be a prototype of polymer/metal/polymer/Si multilayer film which is expected to have wide applications in silicon-based optoelectronic devices.

Experimental Section

The 266 nm radiation from a Nd:YAG laser (Spectra-Physics GCR150-10, 10 Hz, 7 ns pulse duration) was focused onto a PMMA target ($20 \times 20 \times 2$ mm^3, Goodfellow) by using a lens (focal length=300 mm) at an incident angle of 45°. The PMMA target was rotated at 20 rpm by using a standard rotation feedthrough. The laser-induced decomposition of the PMMA sample at 266 nm was studied by using a quadrupole mass spectrometer. The ablation chamber was equipped with a quadrupole mass spectrometer (VG SX300) and pumped by a turbo pump. The base pressure in the chamber was 2×10^{-8} Torr. The ion optics in front of the quadrupole housing were grounded and the ionizer was turned off to detect ionic species. A boxcar averager (SR250) was used to obtain laser-correlated mass spectra. The distance from the target to the detector of the quadrupole mass spectrometer was 21.3 cm. Deposition of PMMA film was done in a He atmosphere on a 10×10 mm^2 Si(100) substrate mounted on a boron nitride heating block. The target-to-substrate distance was 2.5 cm.

Results and Discussion

A neutral mass spectrum obtained by electron impact ionization (including dissociative ionization) of the ablated product at 1.0 J/cm^2 is shown in Figure 1(a). Neutral mass peaks below 20 were not measured due to the large background signal from residual H_2O. The main peaks at 26, 28, 41, 69, and 100 correspond to C_2H_2, C_2H_4, $H_2C=C(CH_3)$, $H_2C=C(CH_3)CO$, and monomer [$H_2C=C(CH_3)CO_2CH_3$]. The smaller peaks at 44, 55, 59, and 85 are assigned to CO_2, C_3H_3O, $COOCH_3$, and $H_2C=C(CH_3)CO_2$. The relative magnitudes of mass peaks were expected to be highly dependent on the laser ablation conditions, like laser fluence, wavelength, and irradiation time, which strongly affect the incubation effects as well as the degradation of the target. No mass peaks above the monomer parent mass were detected up to 300 amu. Our results are in good accord with a previously reported pyrolytic decomposition mass spectra for PMMA,[5] which indicates that the main product of laser ablation of PMMA is MMA. Therefore, it is reasonable to speculate that the pyrolytic decomposition of PMMA leads to depolymerization and monomer (MMA) formation.[9] However, the incubation effect, which could produce fragments of an unsaturated backbone following extensive side-chain scission, can not be completely neglected.[7]

Figure 1(b) shows a cationic mass spectrum (with the electron impact ionizer turned off) at 1.5 J/cm^2, where the major ionic product by laser ablation was C^+. Cationic

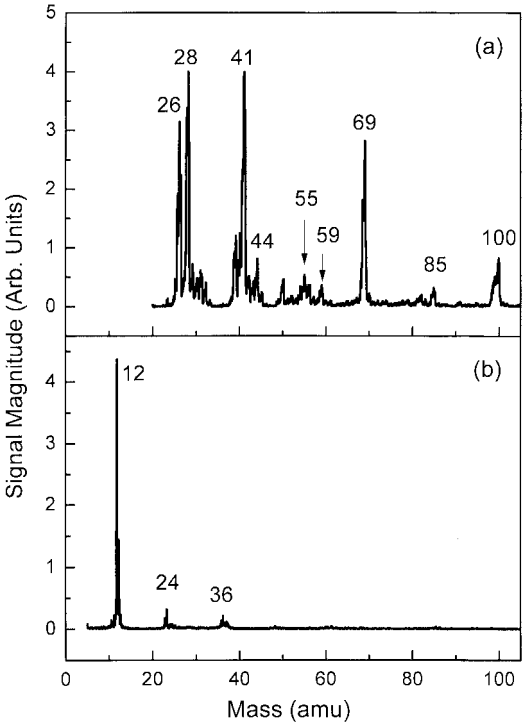

Figure 1. Laser-correlated mass spectra produced by laser ablation of PMMA target (a) neutral mass spectrum with electron impact ionizer on (1.0 J/cm^2), (b) cation mass spectrum with electron impact ionizer off (1.5 J/cm^2).

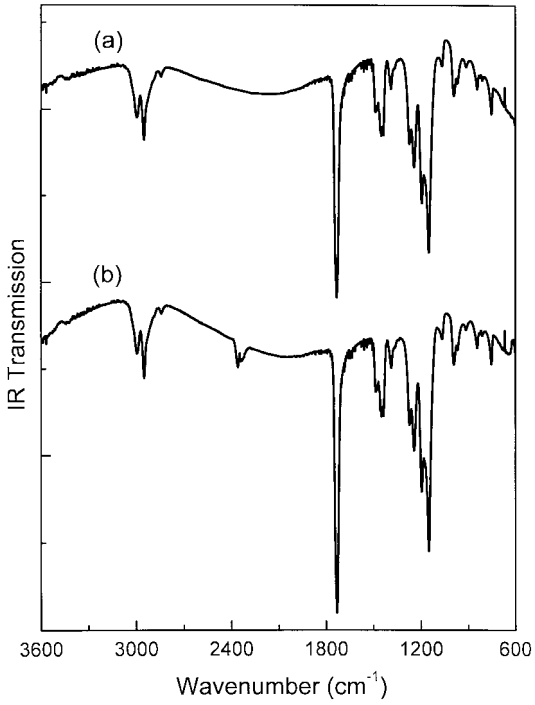

Figure 2. IR spectra of (a) commercial PMMA target (spin-coated film), (b) PMMA film deposited on silicon substrate at 200 °C by laser ablation (200 mTorr, 1.0 J/cm^2).

species were observed only at laser fluences above 1.5 J/cm^2. In our experiments, deposition of PMMA films was performed at 1.0 J/cm^2, where the laser-produced PMMA plume was composed mainly of MMA with no ionic species, according to our mass spectral results. Since the He background pressure is typically 200 mTorr in the deposition experiment, the collisional recombination of monomers in the gas phase plume, which induces formation of dimers and oligomers, may have to be taken into consideration. Also, photofragmentation and collision-induced dissociation of monomers in the plume after ejection by laser ablation are possible.[10]

The deposited PMMA films were analyzed by pyrolysis gas chromatography and IR absorption spectrometry. Surprisingly, the spin-coated and laser-ablated PMMA films gave nearly identical IR spectra as illustrated in Figure 2. In particular, the coincidence of the widths and the positions of the IR absorption peaks of the cast and ablated films are remarkable. The IR spectrum of the laser-ablated film shows characteristic features at ~1200 cm^{-1}, ~1730 cm^{-1}, and ~2950 cm^{-1}, associated with O-CH_3, C=O, and C-H stretchings, respectively. As we varied the He pressure from 50 mTorr to 2 Torr, similar IR spectra were obtained. There was no IR absorption at ~2100 cm^{-1}, which is indicative of the absence of some C≡ C triple bonding observed for hydrogenated amorphous carbon films deposited by laser ablation of PMMA at 193 nm in vacuum.[11] The small absorption peak at ~2350 cm^{-1} is the result of a silicon oxide layer between the deposited PMMA film and Si substrate.

We also attempted PMMA film deposition at different substrate temperatures, ranging from 25 to 200 °C. Repolymerization of MMA on a substrate[9] is possible at temperatures below 0 °C, but the surface morphology is strongly dependent on the substrate temperature. The film deposited at 25 °C appeared hazy. However, the films became more transparent as the substrate temperature was increased above ~100 °C. Also, the film morphology showed significant changes in the neighborhood of the glass transition temperature of PMMA (T_g=105 °C). Figure 3 shows SEM images of PMMA films deposited by laser ablation at 25 and 200 °C. At 25 °C, the film consisted of various sizes of loosely-packed spherical particles; the film deposited at 200 °C was dense and showed better adhesion.[9] The IR spectra of PMMA films deposited at different temperatures were nearly identical. The cross-section analyses provided a measure of the deposition rate at 1.0 J/cm^2, which turned out to be 0.055 nm/pulse.

By a dual target laser ablation method, we have deposited a bilayer film of polymer and metal, that is, PMMA film on Cu layer as shown in Figure 4. Here, a Cu layer was first deposited on a Si substrate by laser ablation of the Cu target at 50 mTorr of He (25 °C, 4.5 J/cm^2). The PMMA film was then formed on the Cu layer by irradiating the PMMA target at 200 mTorr of He (200 °C, 1.0 J/cm^2). As measured by cross-section SEM imaging, the thicknesses of Cu and PMMA layers were 0.1 and 1.0 μm, respectively. Recently, Talaie *et al*. reported a great enhancement of luminescence intensity of poly(2-methoxy, 5-(2'-ethyl-hexyloxy)-*p*-phenylenevinylene) (MEH-PPV) by coating the polymer surface

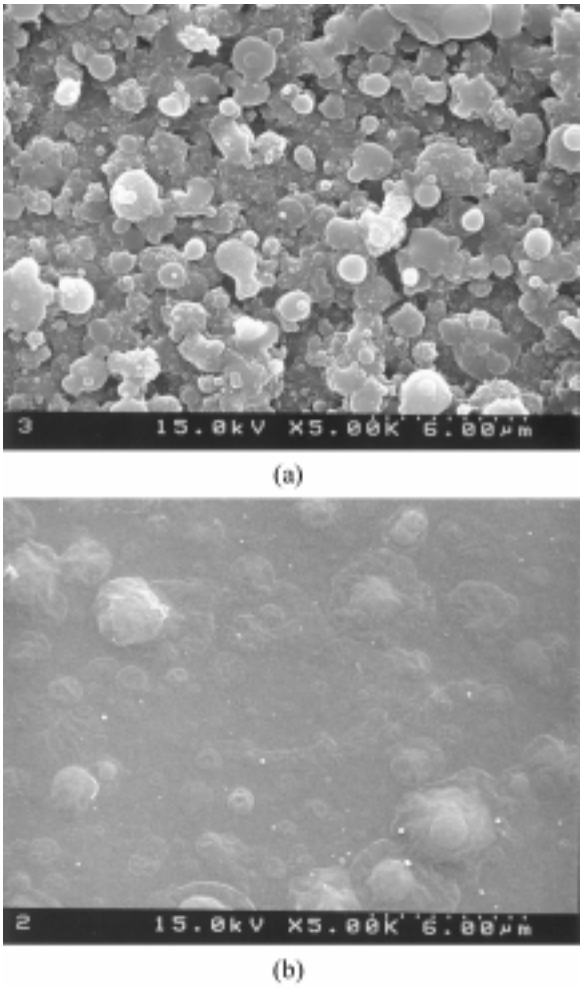

Figure 3. SEM images of PMMA films deposited by laser ablation (200 mTorr, 1.0 J/cm^2) at (a) 25 ^{o}C, (b) 200 ^{o}C.

with transition metals by laser ablation.[12] In this respect, the deposition of Cu film on a pre-deposited PMMA film and co-ablation of the Cu and PMMA targets to fabricate Cu-doped PMMA film are in progress.

In summary, neutral and cationic products formed by laser ablation of PMMA were analyzed by quadrupole mass spectrometry. Monomers and their fragments were the dominant neutral products implying that the material ejection occurs *via* pyrolytic decomposition of PMMA. Also, we have adopted a dual target laser ablation technique and deposited a PMMA/Cu bilayer film successfully.

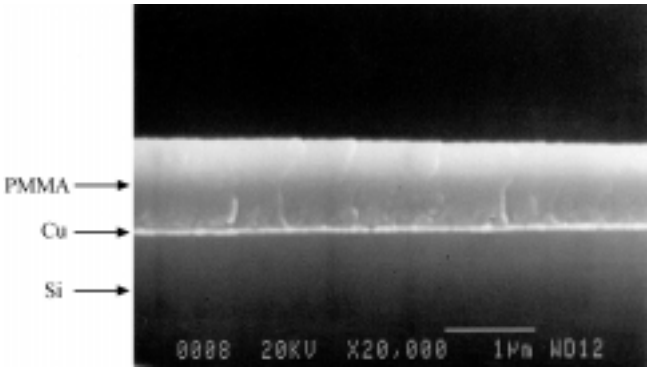

Figure 4. Cross-section SEM image of PMMA/Cu bilayer film deposited on a silicon substrate. Cu layer was deposited at 4.5 J/cm^2 (50 mTorr, 25 ^{o}C). PMMA layer was deposited at 1.0 J/cm^2 (200 mTorr, 200 ^{o}C).

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