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Sputtering of Neutral Molecules and Molecular Ions from the Adenine Crystal Surface Induced by the UV Picosecond Laser Pulse

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This paper presents the results of observation of sputtering of neutral molecules and ions from the crystal adenine surface induced by fourth-harmonic Nd:YAG laser radiation with a pulse duration of 30 ps. The energy fluence of laser pulses was in the region $(1\text{--}3) \times 10^{-4}$ J/cm². The kinetic energy distribution of the sputtered molecules spreads up to 0.7 eV. The experiment shows that the threshold of adenine molecular ion sputtering is connected with absorbed energy density in upper layers of the crystal surface but not by laser radiation intensity.

INTRODUCTION

Previously^{1,2} we reported on observation of molecular ion sputtering of anthracene and DNA bases from a crystal surface induced by nanosecond pulsed UV laser radiation. This radiation wavelength coincides with the electron absorption bands of these crystals. The main feature of the observed phenomenon is its nonthermal nature: heating by laser radiation of a crystal surface under experimental conditions did not exceed 20–50°C. More detailed experiments² with adenine crystals and nanosecond pulses

of the KrF laser ($\lambda = 249$ nm) revealed a strong dependence (F^6) of molecular ion yield on the energy fluence F of laser radiation, and high kinetic energy of molecular ions up to 3 eV. This shows the complex nature of processes resulting in ions sputtering from the crystal surface. Some mechanisms were proposed² to explain ion sputtering but their roles in the process were not appreciated for lack of experimental data.

There are two important questions concerning the observed effect: (a) whether the sputtering threshold is connected with the intensity of laser radiation or its energy fluence; (b) is the neutral molecule sputtering taking place parallel with ion sputtering? This paper presents the results of ion and neutral molecule sputtering from the adenine crystal surface irradiated by picosecond UV laser pulses ($\tau = 30$ ps). These results have been compared with experiments^{1,2} where nanosecond pulses were used. Ions sputtered from the crystal surface were detected by a time-of-flight mass spectrometer. Neutral molecules sputtered from the crystal surface were detected by photoionization by a KrF laser in the volume above the surface.

Experimental setup

Our previous work² describes an experimental setup for the investigation of laser-induced sputtering of ions. A finely dispersed crystalline powder (Zelstofffabrik, Waldhof) was placed on the repellent electrode of the time-of-flight mass spectrometer ion source. A single picosecond pulse of fourth-harmonic Nd:YAG laser radiation of 266 nm wavelength was directed at the sample on the 10° angle to the plane of the repellent electrode (Figure 1). The sputtered ions repelled from the ion source region by the electric pulse of 125 V/cm and after mass separation in the time-of-flight mass analyzer were recorded with an electron multiplier. The signal from the multiplier was recorded by a memory oscilloscope.

To detect the sputtered neutral molecules the time-delayed KrF laser pulse was used to photoionize sputtered molecules above the surface. Molecular photoionization was effected according to the two-step scheme³ through an intermediate electron-excited state, because the KrF laser photon energy equals 5 eV and the ionization potential of the adenine molecule is 8.3 eV.⁴ The KrF laser pulses were focused by a quartz lens $f = 0.4$ m, the focus region was at a distance of 4 mm above the sample. The energy fluence of the pulses in the focus region was 0.5–1 J/cm². The KrF laser pulse delay time with respect to the UV picosecond laser pulses irradiating the adenine crystal surface was varied in the region (2–10) μ s.

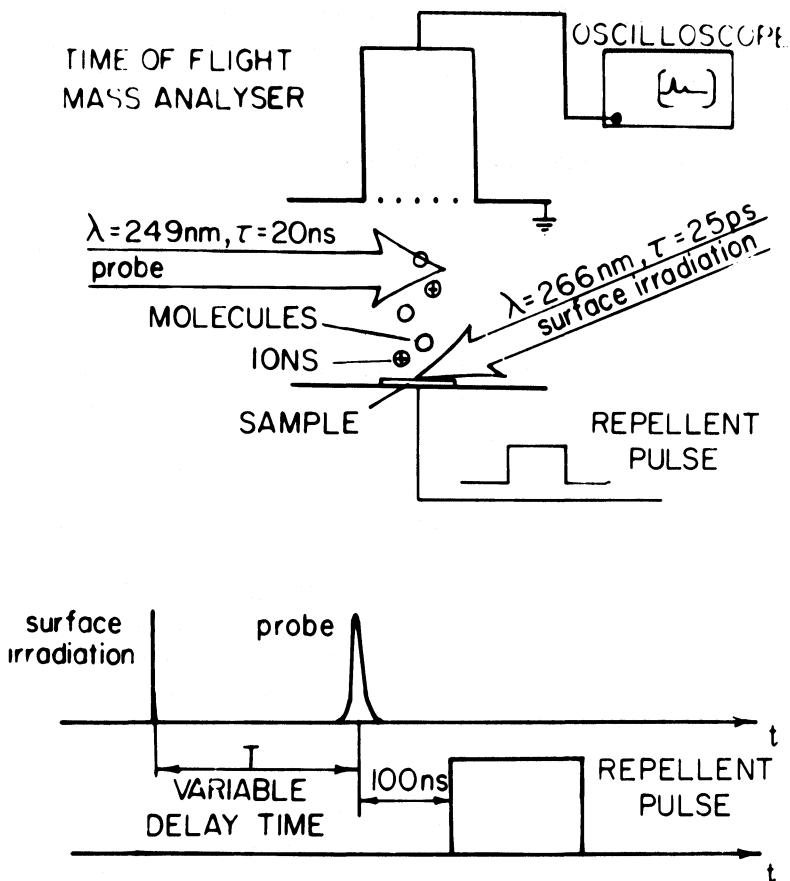


FIGURE 1. Scheme of the experiment. The lower portion is a time diagram of laser pulses and of the repellent electric pulse.

This allowed measurement of the velocity distribution of sputtered molecules in the region $(4-20) \times 10^4 \text{ cm/s}$.

The time-of-flight mass spectrometer had a resolution of 200 at a half-level amplitude. The mass identification accuracy for the ions sputtered from the crystal surface equalled plus or minus 1 a.u. For the molecules ionized by KrF laser above the surface the mass identification accuracy was plus or minus 7 a.u. This is connected with the nonoptimal working regime of the mass spectrometer in case of simultaneous detection of ions

sputtered from the surface and ions formed as a result of photoionization of molecules above the surface. The residual gas pressure in the mass spectrometer was 10^{-7} Torr. Oil-free pumping was used for evacuation.

Experimental results and discussion

Investigation of mass spectra of ions resulting from picosecond pulse ($\tau = 30$ ps, $\lambda = 266$ nm) irradiation of adenine crystals shows that as in the case of Ref. 2, where KrF laser pulses ($\tau = 20$ ns, $\lambda = 249$ nm) were used, the dominant component is a molecular ion. The sputtered ion yield, as in Ref. 2, had a strong dependence on the laser pulse energy fluence. Exact measurements of the sputtered ion yield dependence on the picosecond pulse energy fluence was difficult for the fluctuations of spatial energy distribution in the laser beam. The important difference is the lower threshold of 1.5×10^{-4} J/cm² for the ion sputtering with respect to the threshold of 8×10^{-4} J/cm² in the case of $\lambda = 249$ nm, $\tau = 20$ ns. But in the last case the absorption coefficient of the adenine crystal for the wavelength of 249 nm ($K_{249} = 3.8 \times 10^4$ cm⁻¹) is four times less than that for $\lambda = 266$ nm ($K_{266} = 1.6 \times 10^5$ cm⁻¹).⁵ Taking into account this fact, one can conclude that the threshold of absorbed energy density for the molecular ion sputtering is the same for both cases, though the intensity of the picosecond laser pulse was of two orders of magnitude higher than that of the nanosecond one. It follows from the analysis of time duration of the molecular ion signal that as in Ref. 2 the kinetic energy distribution of the sputtered ions spreads up to several eV.

Figure 2 shows the multiplier signal corresponding to the mass spectrum region near the adenine molecular ion. The oscillogram A was obtained when the sample crystals had been irradiated by the picosecond pulse of the fourth-harmonic Nd:YAG laser with energy fluence 2.5×10^{-4} J/cm². The signal amplitude is equal to 10^2 ions per pulse. The B oscillogram was obtained when only KrF laser pulses focused above the surface were used. The small signal in this case is related to the photoionization of organic molecular background and adenine vapor. The C oscillogram was obtained when both laser pulses with delay time between them $\Delta t = 4\mu\text{s}$ were used. At the same time as the pulse corresponding to adenine molecular ions sputtered from the surface, an additional pulse can be seen corresponding to the photoions obtained from the neutral molecules above the surface. This last pulse depends on the KrF laser energy fluence as $F^{1.5}$. The deviation from the square law dependence apparently is related

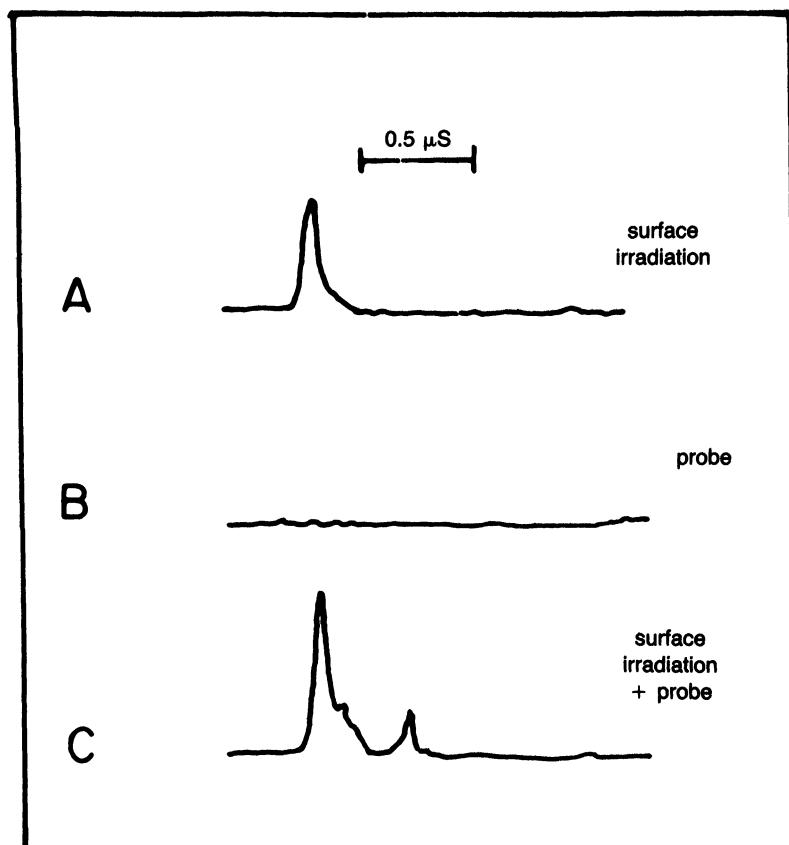


FIGURE 2. Oscillograms of electron multiplier signals. (A) the crystal surface being irradiated, $\lambda = 266$ nm, $\tau = 30$ ps. (B) the KrF laser pulses probing above the surface, $\lambda = 249$ nm, $\tau = 20$ ns. (C) both pulses used with delay time of 4 μ s.

to the saturation of the two-step photoionization yield at the energy fluence $F = 0.5 \text{ J/cm}^2$. Based on the ions, time-of-flight estimations of sputtered neutral molecular mass give $m = (140 \pm 7)$ a.u., which equals the adenine molecular mass of 135 a.u. within the range of experimental error. Taking into account the less efficient detection of neutral molecules, one can conclude from Figure 2C that the number of sputtered adenine molecular ions is approximately equal to the sputtered molecules. But when the energy of the irradiating laser pulses decreases the number of sputtered molecules

decreases more slowly than that of ions. This leads to the predominance of the neutral molecule sputtering process. As laser energy is increased the ion sputtering process becomes dominant.

Figure 3 shows the velocity distribution of the sputtered molecules in the region $(4-20) \times 10^4$ cm/s. This distribution was measured by variation of delay time of KrF laser pulses time-delayed with respect to the picosecond pulses irradiating the surface in the region of $(2-10)$ μ s. Calculating the velocity, it was suggested that after the irradiation of the crystal surface the sputtering process had been proceeding less than 1 μ s. Figure 3 shows that maximum velocities of the sputtered molecules were up to 10^5 cm/s, i.e., corresponding to 0.7 eV. The dotted line represents the Maxwell velocity distribution of molecules with $t = 1250^\circ\text{C}$. But according to the estimation, the heating of the crystal surface under experimental conditions does not exceed 30°C . This estimation suggests that the absorbed laser

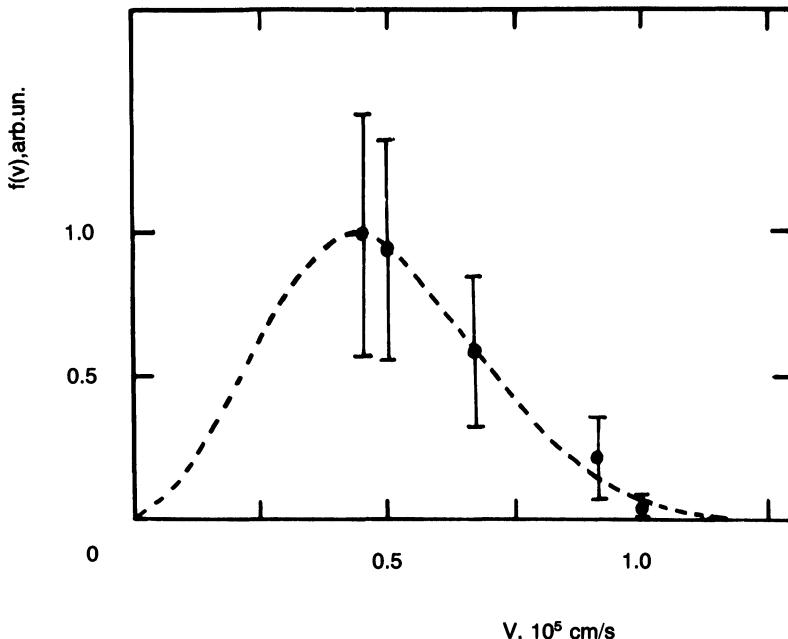


FIGURE 3. Velocity distribution of the sputtered neutral molecules. The dotted line represents the Maxwell distribution with $t = 1250^\circ\text{C}$.

energy is thermolized in the upper layers of the adenine crystals. This fact points out the nonequilibrium nature of molecular sputtering.

CONCLUSIONS

The experimental results have shown that for the case of picosecond irradiation ($\lambda = 266$ nm) of the adenine crystal the energy fluence threshold of molecular ions is five times lower than that of experimental conditions in work where the nanosecond KrF laser pulses ($\lambda = 249$ nm) were used.² But taking into consideration the difference of absorption coefficients for the radiation with $\lambda = 249$ nm and $\lambda = 266$ nm, the absorbed energy density threshold was the same in both cases.

Near the threshold of ion sputtering the sputtering of neutral molecules with mass $m = 140 \pm 7$ a.u. (near the adenine mass $m = 135$ a.u.) was observed. When the energy fluence of picosecond laser pulses was in the region $1 \pm 2 \times 10^{-4}$ J/cm² the number of sputtered neutral molecules exceeded the number of ions, but with an increase of pulse energy fluence ion sputtering became dominant.

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