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LOW-FLUENCE LASER INDUCED FRAGMENTATION AND DESORPTION OF 3,4,9,10-PERYLENETETRACARBOXYLIC DIANHYDRIDE (PTCDA) THIN FILM

Laser-induced fragmentation and desorption of fragments of PTCDA films vacuum-deposited on GaAs (100) substrate has been studied by time-of-flight (TOF) mass spectroscopy. The main effect caused by pulsed laser light irradiation (pulse duration: 10 ns, photon energy: 2.34 eV and laser fluence ranging from 0.5 to 7 mJ/cm²) is PTCDA molecular fragmentation and desorption of the fragments formed, whereas no desorption of intact PTCDA molecule was detected. Fragments formed are perylene core $C_{20}H_8$, its half $C_{10}H_4$, carbon dioxide, carbon monoxide and atomic oxygen. All desorbing fragments have essentially different kinetic energy. The mechanism of photoinduced molecular fragmentation and desorption is discussed.

Keywords: PTCDA, Photochemistry, Laser-induced desorption, Surface dynamics.

For the last decades thin organic films attract much attention due to their wide ongoing and potential applications in science and technology [1-4]. Particularly interesting are the photoinduced effects governing the properties of photochemical, opto- and nanoelectronic devices, chemical sensors, light-emitting diodes, field-effect transistors and solar cells based on such films [5-7]. In relation to this the aim of the present study is elucidation of the character and the mechanism of interaction of pulsed laser light with the films of PTCDA – material which is widely explored in various applications [1-5]. Unlike the vast majority of works in this direction when the main effect is laser ablation of polymer films [5-9] the focus of the present work is to investigate the low laser fluence effects when the properties are presumably determined by valence electronic transitions. For this purpose nanosecond pulsed laser light with fluence in the range of 0.5 – 7 mJ/cm² and photon energy of 2.34 eV exceeding PTCDA band gap (2.1 eV) to generate hot carriers was used. The photoinduced effect was investigated by time-of-flight (TOF) mass spectroscopy which allows monitoring possible photoinduced desorption of the molecule and its fragments. The TOF mass-spectroscopy technique has an advantage to detect the desorbed specie not altered by an electron impact used for example in quadrupole mass-spectrometer. Moreover it allows simultaneous detection of wide range of masses for a single laser shot, as well as determination of the velocity distribution

of desorbing specie. Using of the laser light with well defined photon parameters offers an advantage of gaining the most straightforward and unambiguous information about the photoinduced phenomena under investigation.

The measurements have been carried in ultra high vacuum chamber (base pressure: ca. 10^{-9} Torr) with the aid of TOF mass spectrometer equipped with a flight tube of ca. 1 meter long as shown in Fig. 1. The advantage of the time-of-flight technique used is that it allows distinguishing between the fragments produced on the sample and the artificial fragments produced by electron impact in an ion source (4). Desorbed specie moving along the surface normal pass through the two drifting regions (2 and 3). In the first region the neutral specie are separated according to their initial kinetic energy and reach the ion source (4) of time-of-flight mass-spectrometer. The groups of specie of different mass

but with the same initial kinetic energy formed in the ion source are additionally supplied with the same amount of energy. The specie are mass selected in the second drifting region (3) and are detected by secondary electron amplifier (5).

The laser fluence was kept as low as 0.5-7 mJ/cm² to avoid possible thermal effect which might obscure the effects produced by photoinduced electronic transitions. Pulse duration and the photon energy of the laser beam were 10 ns and 2.34 eV, respectively. The laser beam was focused on a sample to a spot of ca. 10^{-3} cm² area at incidence angle of 45°. The sensitivity of the spectrometer corresponds to $(2-5)10^{-5}$ monolayer. The PTCDA film of 100 nm thick was formed by thermal evaporation in high vacuum on widely used for this purpose GaAs(100) crystal [10], after which the specimen was transferred into the UHV chamber (base pressure: c.a. 10^{-9} Torr)
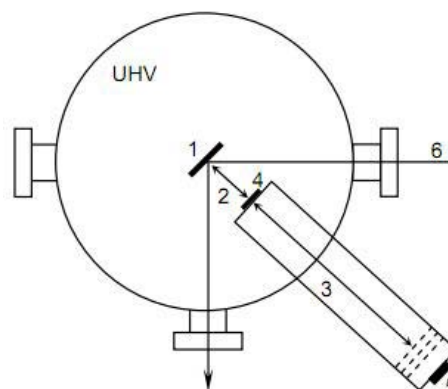

Fig. 1. Schematic view of experimental setup for photoinduced time-of-flight measurements: 1 – specimen; 2, 3 – first and second drifting spaces where the desorbed specie move; 4 – ion source, where the desorbed specie are ionized by electron impact; 5 – detector, 6 – laser beam

for laser induced measurements. The film thickness was measured by quartz microbalance and verified ex-situ by atomic force microscope (Ntegra-Aura, NT-MDT). The typical scan and height profile are shown in Fig. 2 revealing rather uniform lateral large-scale film thickness and absence of open substrate regions.

To clean the surface of the PTCDA film from the residual gas molecules a number of laser shots of fluence lower than the PTCDA fragmentation and desorption threshold was applied. The corresponding mass spectrum of the residual gas molecules at low laser fluence (0.8 mJ/cm²) is shown in Fig. 3. curve 1. Subsequent laser fluence increase (2 to 7 mJ/cm²) leads to dramatic transformation of the spectra due to PTCDA molecular fragments desorption (Fig. 3, curves 2, 3). The features at m/z = 28, 44 correspond to CO and CO_2, respectively. Almost similar signal intensity in both cases suggests that extraction and decomposition of PTCDA carboxylic terminals with subsequent

CO and CO_2 desorption occurs upon laser light effect. At the same time, as seen in Fig. 3, curves 1, 2, slightly higher CO signal intensity over that of CO_2 and especially appearance of atomic oxygen desorption signal (m/z = 16) points at the dissociation of part of CO_2 molecules during photoinduced decomposition of carboxylic terminals.

Another dominant feature seen in the spectra (Fig. 1. curves 2, 3) is appearance of heavier molecular fragments at m/z = 248 and 124 which correspond to perylene core of the molecule $C_{20}H_8$ and its half $C_{10}H_4$, respectively. No desorption of an intact PTCDA molecule (m/z = 392) was detected at all experimental conditions studied. The latter provide an evidence that the photofragmentation and desorption mechanism is non-thermal. This assumption is based on the fact that the sublimation temperature of PTCDA is in the range of 350 to 450°C which is not enough to brake the intramolecular chemical bonds [11]. The lowest bonding energy in PTCDA molecule (3.6 eV) corresponds to single

C–C bonds between perylene core and carboxylic group. The single C–O bond has about the same energy (3.75 eV), whereas the C–C bonding energy in aromatic ring is 5.3 eV and the double C–O bond has energy of 7.8 eV [10]. Two naphthalene molecules are bound to each other with two C–C bonds of energy of 4.2 eV which is lower than the corresponding energy in aromatic ring (5.3 eV) [12]. Comparing these PTCDA chemical bond energies with the photon energy used (2.34 eV) one can assume that the fragmentation and desorption mechanism is due to the photoinduced electronic transitions rather than to the thermal effect. One can suggest the following mechanism. Photon irradiation of PTCDA effectively produces electron-hole pairs since the photon energy is higher than the PTCDA band gap (c.a. 2.1 eV) [13]. Subsequent electron-hole recombination is more efficient at the defect and electron density gradient sites [5], among which are the region of carboxylic terminals due to charge transfer from carbon to oxygen atom. The latter may cause the corresponding $C_{20}H_8$–C_2O_3 bond breaking and carbon mono- and dioxide desorption, as observed in Fig. 3, curves 2,3. However, the recombination energy (c.a. 2.1 eV) is lower than the corresponding intermolecular bond energy between perylene core and carboxylic group which is 3.6 eV. Therefore one can expect that the multi-electron and multi-photon effects are operative, when the bond braking occurs upon simultaneous recombination of two electron-hole pairs at the same site or deexcitation of an electron-hole pair excited to an energy multiple to 2.34 eV due to multi-photon process, as discussed for instance in [14, 15]. In favor of this assumption is the observed fact that the fragmentation and desorption intensity notably grows with increase of laser fluence which leads to increase of electron-hole concentration and multiphoton effect cross-section (Fig. 3, curves 2, 3). Even at two-photon process the deexcitation energy (4.68 eV) is enough to break the bond between the carboxylic group and the molecular core (3.6 eV) to release CO, CO_2, and $C_{20}H_8$, as well as to cleave the core into $C_{10}H_4$ fragments. It should be noted that the observed PTCDA photoinduced
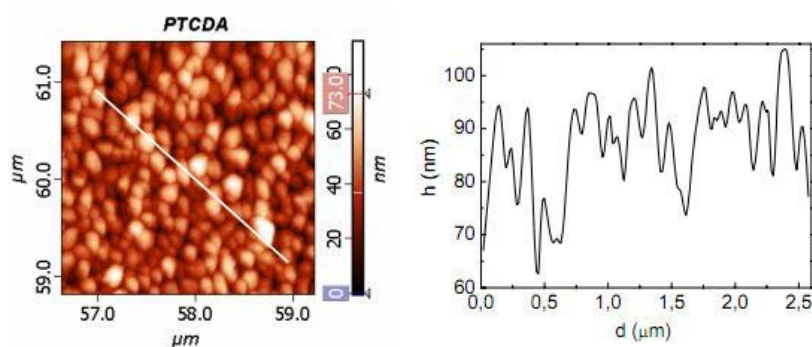

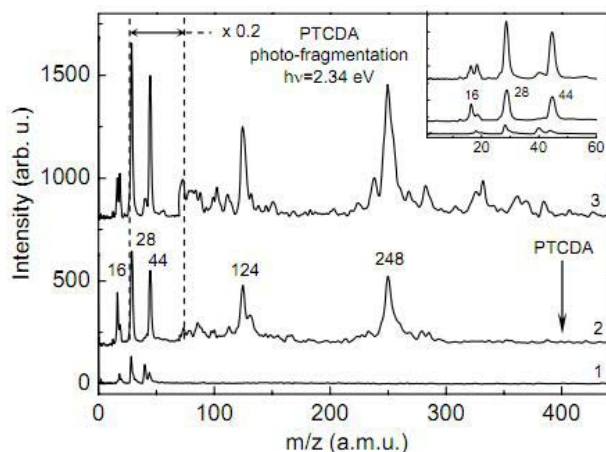Fig. 2. AFM image and height profile of PTCDA film on GaAs(100)

Fig. 3. Mass-spectra of PTCDA fragments desorbed under laser irradiation. Laser fluence, mJ/cm²: 1 – 0.8; 2 – 4; 3 – 7. Detail spectral features in (0 – 60) a.m.u. region are shown in an inlay

fragmentation path is essentially different from that observed upon heating when the dominant feature in thermal desorption flux is an intact PTCDA molecule [16]. Additional evidence of non-thermal mechanism of PTCDA fragmentation and desorption is provided by time-of-flight measurements. The corresponding TOF spectra reflecting distribution of initial kinetic energies of desorbing fragments are shown in Fig. 4.

The main evidence provided by these distributions is that the kinetic energies of the desorbing specie are essentially different from each other: In case if the energies of the fragments are the same one should expect longer flight time for heavier species. In the present, case as follows from Fig. 4, the kinetic energy of the desorbing fragments increase in the sequence:

$$O - CO - CO_2 - C_{10}H_4 - C_{20}H_8.$$
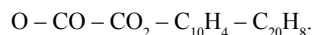
This trend is in lines with the possible energy deexcitation pathways which occur after photoexcitation of the molecule. The photon excites the π-system of the perylene core producing the corresponding electron-hole pairs. Deexcitation energy breaks the intermolecular bonds of π-conjugated PTCDA molecule and the bonds between the perylene core and carboxylic terminals. Since the energy of the multi-photon (or even two-photon) excitation is higher than the corresponding intermolecular binding energies the excess energy is supplied to the fragments in the form of kinetic energy causing their desorption from the surface of PTCDA film. Another deexcitation pathway is cleavage of entire perylen core $C_{20}H_8$ into two fragments $C_{10}H_4$, in which case lower energy is supplied to cause desorption of the $C_{10}H_4$ fragments, in lines with the observed lower energy of desorbed $C_{10}H_4$ compared to $C_{20}H_8$. Regarding the CO and CO2 specie, one can assume that they are formed as a result of destruction of unstable dicarboxylic group C_2O_3 released into vacuum after photoinduced fragmentation of PTCDA molecule. The evidence is provided by almost identical TOF distribution of CO and CO_2, as seen in Fig. 4, as a result of essentially the same velocity of CO and CO_2 fragments. Slightly lower CO_2 intensity is presumably due to its dissociation into CO and O,
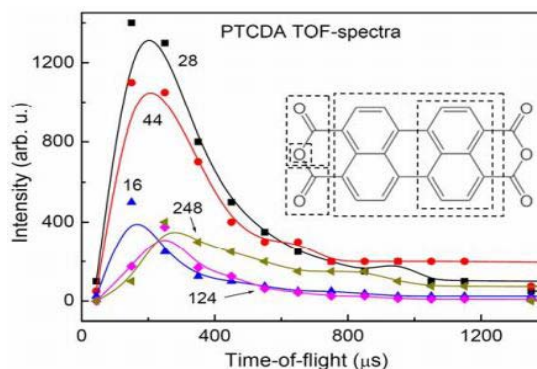

Fig. 4. Time-of-flight spectra of fragments photodesorbed from PTCDA film, a.m.u.: 16 – atomic oxygen, 28 – CO, 44 – CO_2, 248 and 124 – perylene core $C_{20}H_8$ and its half $C_{10}H_4$, respectively. Inlay: fragmentation scheme of PTCDA molecule

of which evidence is appearance of signal corresponding to atomic oxygen, $m/z = 16$ (Fig. 3). The fact the atomic oxygen has lowest kinetic energy, as seen in Fig. 4, can be reconciled assuming that initial photoexcitation which occurs in π-system of the perylene core efficiently quenches within the perylene core itself and perylen-carboxylic groups before it reaches the peripheral region of oxygen specie. Taking into account above considerations the photofragmentation scheme of PTCDA molecule is shown in Fig. 4.

Pulsed nanosecond laser light of photon energy of 2.31 eV and low fluence ranging from 0.5 to 7 mJ/cm² cause fragmentation of PTCDA 100 nm thin film vacuum-deposited onto GaAs(100) and desorption of fragments. Measurements carried out by time-of-flight mass spectroscopy reveal that the main photoinduced fragments formed are perylene core $C_{20}H_8$, its half $C_{10}H_4$, carbon dioxide CO_2, carbon monoxide CO and atomic oxygen. No desorption of an intact PTCDA molecule was detected whereas, according to literature data, this is the main feature observed for thermal desorption of PTCDA. Time-of-flight measurements reveal that the fragments photodesorbed from the film have essentially different kinetic energies indicating that the dominant bond breaking mechanism is essentially non-thermal, presumably induced by valence electronic transitions.

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