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Raman spectroscopy of the PTCDA–inorganic semiconductor interface: evidence for charge transfer

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Abstract

In the present work, we investigate the vibrational properties of a PTCDA molecule with an additional positive or negative charge using density functional theory. With respect to the calculated vibrational frequencies of the neutral molecule, some modes in particular in the region 1200–1800 cm^{-1} show large shifts. These calculations are compared with resonant Raman spectra of sub-monolayer PTCDA films on passivated semiconductor surfaces, both before and after annealing the deposited films at elevated temperatures (350 °C). Independent of the sample treatment, the sub-monolayer Raman spectra correspond quite well to reference spectra obtained for thicker films, and we find no evidence for the strong shifts predicted in the calculations for the charged species. From the small changes in the mode frequencies it can be concluded that any charge transfer present involves significantly less than one elementary charge. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: PTCDA; Charge transfer; DFT; Raman spectroscopy

1. Introduction

In epitaxial films of 3,4,9,10-perylene tetracarboxylic dianhydride (PTCDA), the molecules are expected to interact strongly along the stacking direction, while their interaction with the underlying substrates can be considerably weaker. For ultrathin PTCDA films deposited on semiconductor or metal substrates, this interaction can be investigated using vibrational techniques, such as Raman, infrared or high resolution electron energy loss spectroscopy, revealing changes between thick films and the sub-monolayer regime [1,2]. Experimental findings can be compared with quantum chemical investigations of the vibrational properties of a single molecule [2,3].

The most common explanation of observed changes is charge transfer between substrate and deposited molecules. There are two possible mechanisms of charge transfer: firstly, formation of new covalent or ionic bonds, and secondly charge transfer accompanied by an interface dipole without formation of bonds. Photoemission studies performed for PTCDA deposited on a Se-passivated GaAs substrate [4] reveal that changes in lineshape of the core level emission from Ga, As and Se substrate features are very subtle. Therefore, the formation of new bonds between PTCDA and the Se-passivated GaAs substrate can be excluded and the interface may be considered to be chemically unreactive. However, there is an interface dipole, which induces a negative charge to PTCDA molecules. The

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second possibility can be investigated with the computation of the vibrational spectra of a single molecule in differently charged states. For this purpose, the GAUSSIAN98 package [5] using the B3LYP density functional and the 3-21G basis set is employed. The calculated vibrational properties of PTCDA with an additional charge are based on optimized geometries for the molecular anion or cation.

2. Experimental

The PTCDA films were prepared by organic molecular beam deposition (OMBD) as described elsewhere in more detail [1,4]. The p-type Si(1 1 1) substrates were cleaned by etching for 2 min in hydrofluoric acid (HF, 40%). The surface quality was checked by low electron energy diffraction and Auger spectroscopy. Passivated GaAs(1 0 0) surface was prepared by a two-step procedure under UHV conditions. Arsenic-capped n-type GaAs(1 0 0) was heated to 380 °C followed by heating to 450 °C and simultaneous exposure to Se resulting in a Se-passivated GaAs(1 0 0)-2 × 1 surface. Prior to OMBD, the PTCDA source material was purified by thermal gradient sublimation in high vacuum. The thickness of a reference sample as determined with atomic force microscopy (40 nm) was used for the calibration of the deposition rate. For the sub-monolayer samples, the nominal coverage of 0.5 ML was estimated from the ratio of the deposition times with respect to this thick film reference.

All Raman spectra were excited by an Ar$^+$ laser using the 488 nm (2.54 eV) line with a power of 20 mW and recorded by a triple monochromator Raman spectrometer (Dilor XY) equipped with a CCD camera for multichannel detection.

Table 1
B3LYP/3-21G calculations of Raman-active vibrational modes of neutral molecule, anion and cation. For the A_g modes visualized in Fig. 1, the root-mean-square deviation between measured and calculated modes is 17 cm^{-1}. The experimental assignments of the B_{3g} modes are taken from [6]

Experimental values (Raman spectra, cm^{-1})	Symmetry assignment	B3LYP/3-21G		
		Neutral (cm^{-1})	Δ_{anion} (cm^{-1})	Δ_{cation} (cm^{-1})
233	A_g	233	1	0
265	B_{3g}	255	3	−1
388	A_g	389	4	−1
394	B_{3g}	399	−5	−4
431	B_{3g}	437	−4	−3
476	A_g	476	−4	0
538	A_g	539	−4	1
562	B_{3g}	598	−9	−6
625	A_g	627	6	−6
	B_{3g}	701	−2	−4
724	A_g	732	−3	−3
856	A_g	853	−3	0
868	B_{3g}	866	−2	−14
1025	B_{3g}	1026	−22	17
1050	A_g	1059	−7	4
1071	B_{3g}	1075	3	−1
1140	B_{3g}	1196	−2	−2
1149	A_g	1151	4	−2
1159	B_{3g}	1232	7	−8
1240	B_{3g}	1254	14	−4
1280	A_g	1269	12	7
1303	A_g	1346	−18	−16
1322, 1335, 1345	B_{3g}	1355	15	28
1381	A_g	1363	9	−3
1390	A_g	1389	16	17
1451	A_g	1472	1	12
1462	B_{3g}	1504	−10	−9
	B_{3g}	1554	−2	3
1572	A_g	1591	−18	−11
1590	A_g	1620	−8	−15
1615	B_{3g}	1634	−61	−66
	B_{3g}	1756	−97	−23
1773	A_g	1800	−85	−8

3. Results

Table 1 shows experimental and calculated frequencies of Raman-active in-plane modes (A_g and B_{3g}) together with the symmetry assignments. The subsequent columns present the relative changes in frequencies of the vibrational modes for a charged molecule, where the correspondence with the vibrational modes of the neutral species is derived from the similarity of eigenvectors. Whenever possible, the calculated frequencies are assigned to experimental features, as discussed elsewhere in more detail [6]. In Fig. 1, the assignment of the A_g modes is visualized for the Raman spectrum obtained on the 40 nm reference sample. Fig. 2 compares the different sub-monolayer samples with the thick film reference and the calculated mode frequencies. Due to signal-to-noise limitations, the sub-monolayer spectra are displayed only in the region of the largest Raman features.

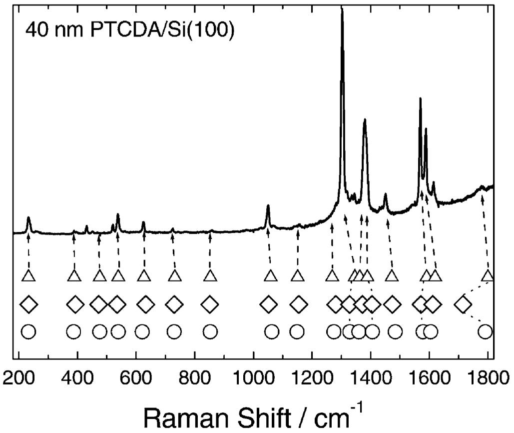

Fig. 1. Resonant Raman spectrum of 40 nm PTCDA film on Si(1 0 0) and calculated A_g frequencies for neutral (△) PTCDA, and negatively (◇) and positively (○) charged molecules.

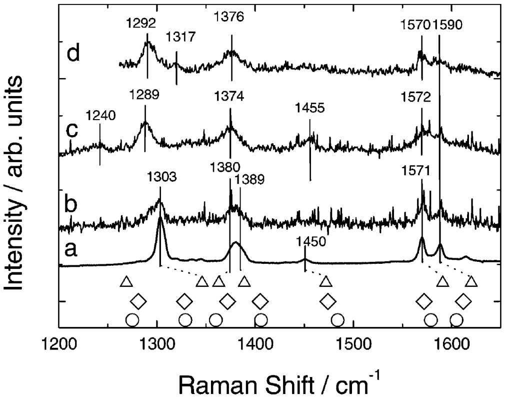

Fig. 2. Resonant Raman spectra of PTCDA: (a) 40 nm PTCDA film on Si(1 0 0); (b) ~0.5 ML PTCDA film on Si(1 0 0); (c) ~0.5 ML PTCDA/Si(1 0 0) annealed at 350 °C; (d) ~0.5 ML PTCDA/Se-GaAs(1 0 0) annealed at 350 °C. The calculated A_g modes for neutral and charged molecule are shown with the same signs as in Fig. 1.

4. Discussion

The most dominant features occurring in the resonant Raman spectrum of the thick film can all be assigned to A_g modes, compare Fig. 1 [3]. For the region below 1000 cm^{-1}, there is an obvious one-to-one correspondence between calculated and observed features. In the region (1200–1700 cm^{-1}) displayed in Fig. 2 with the most pronounced modes, the well known systematic deviations of the mode frequencies calculated with density functional methods make the assignment more difficult, especially for modes with strong C–H bending character. However, even for modes with rather large deviations between the calculated position and the corresponding observed mode frequency, we expect that the shift between neutral and charged molecules should be reproduced quite well. The A_g frequencies calculated for the neutral molecule are in good agreement with the observed Raman-active modes of the reference sample, resulting in a root-mean-square deviation of 17 cm^{-1} without any correction factors.

The Raman spectrum of a 0.5 ML PTCDA film on H-passivated Si(1 0 0) substrate reveals all the dominant A_g features of the PTCDA thick film without any marked shift. Therefore, neither formation of new bonds nor a full electron charge transfer is observable. After annealing at 350 °C some changes in the Raman spectrum can be seen, e.g. the vanishing of the most pronounced mode at 1303 cm^{-1} and the appearance of modes at about 1240 and 1289 cm^{-1}. The spectrum of an annealed sub-monolayer PTCDA film deposited on the Se-passivated GaAs(1 0 0) surface looks similar to the annealed film on a passivated Si(1 0 0) surface. Photoemission spectroscopy measurements do not reveal changes in lineshape of the core levels of Ga, As, while the Se core level emission changes indicate a loss of Se atoms on top of the surface upon annealing [4]. In the case of a new covalent bond formation one would in addition expect a shift towards higher or lower binding energy.

The Raman mode at 1240 cm^{-1} can be attributed to the calculated B_{3g} mode at 1254 cm^{-1} (cf. Table 1). For the mode at 1289 cm^{-1} seen for annealed samples, there are two possibilities: firstly, this mode could correspond to the bulk-like mode at 1303 cm^{-1} which is shifted, or, secondly, it could arise from a redistribution of intensity from this most prominent mode to the neighboring A_g mode at lower frequency, calculated to occur at 1269 cm^{-1}. In any case, the smallness of the observed changes confirms the conclusion from photoemission spectroscopy [4] that the interaction between PTCDA molecules and semiconductor substrate remains very weak.

Concerning the calculated vibrational modes of anion and cation, we focus on the region 1200–1700 cm^{-1}, where the Raman features have been measured. For the calculated shifts of a charged

PTCDA molecule with respect to the neutral molecule (Table 1) there is no one-to-one correspondence with the changes in the measured Raman spectra. For example, the experimental modes at 1303 and 1451 cm^{-1} are shifted in the same direction for both the anion and cation calculation, while for the mode at 1381 cm^{-1} the direction of shift agrees only for the cation calculation. For the modes at 1390, 1572 and 1590 cm^{-1} the direction of shifts does not agree at all with the results of the calculations. In addition, the appearance of the well pronounced C=O stretch modes in the region from 1550 to 1600 cm^{-1}, discussed in [2], due to charge transfer is not detected for our samples. From the photoemission measurements it is known [4] that the interface dipole is induced by a negative charge transferred to the PTCDA molecule, which is much lower than the elementary charge. From our Raman spectroscopy studies supported by the photoemission spectroscopy results we conclude that there is no transfer of an entire elementary charge per molecule between PTCDA and passivated semiconductors surfaces such as Si and GaAs and other mechanisms have to be responsible for the changes in the Raman spectra.

If charging of the molecules can be excluded, another possible origin for changes in the Raman spectra of the annealed sub-monolayer PTCDA films on passivated semiconductor surfaces is a small geometric distortion, like a bending of the molecule. A hint for this suggestion is the appearance of a B_{3g} mode at 1240 cm^{-1}. Such a bending can occur due to a rearrangement of the PTCDA molecule with respect to the substrate superstructure. Unfortunately, for the time being, these more subtle geometric changes have not yet been studied with microscopic calculations. Based on such more involved computational investigations of molecule and substrate surface together, the small changes occurring in the vibrational spectra in the monolayer regime could be assessed with higher precision.

5. Summary

Thin films of PTCDA grown on passivated semiconductor surfaces have been studied by means of resonant Raman spectroscopy. The Raman spectra of sub-monolayer films do not show any changes due to the formation of new bonds, and even after annealing, the observed changes in the Raman frequencies remain small. From ab initio calculations performed on charged PTCDA molecules, we expect larger shifts of the mode frequencies, excluding any significant charge transfer in the samples studied. We suppose that the spectral changes are due to small geometric distortions of the molecules in the annealed films which leads to a redistribution of scattering intensities between different modes.

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References

[1] T.U. Kampen, G. Salvan, M. Friedrich, D.A. Tenne, S. Park, D.R.T. Zahn, Appl. Surf. Sci. 166 (2000) 387.

[2] F.S. Tautz, S. Sloboshanin, J.A. Schaefer, R. Scholz, V. Shklover, M. Sokolowski, E. Umbach, Phys. Rev. B 61 (2000) 16933.

[3] R. Scholz, A.Yu. Kobitski, T.U. Kampen, M. Schreiber, D.R.T. Zahn, G. Jungnickel, M. Elstner, M. Sternberg, Th. Frauenheim, Phys. Rev. B 61 (2000) 13659;
R. Scholz, A.Yu. Kobitski, T.U. Kampen, M. Schreiber, D.R.T. Zahn, G. Jungnickel, Th. Frauenheim, Phys. Stat. Sol. (b) 221 (2000) 541.

[4] S. Park, T.U. Kampen, D.R.T. Zahn, W. Braun, Appl. Phys. Lett. 76 (2000) 3200;
S. Park, T. Querner, T.U. Kampen, W. Braun, D.R.T. Zahn, Appl. Surf. Sci. 166 (2000) 376.

[5] Gaussian 98 (Revision A.1), M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, V.G. Zakrzewski, J.A. Montgomery, R.E. Stratmann, J.C. Burant, S. Dapprich, J.M. Millam, A.D. Daniels, K.N. Kudin, M.C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G.A. Petersson, P.Y. Ayala, Q. Cui, K. Morokuma, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J. Cioslowski, J.V. Ortiz, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P.M.W. Gill, B.G. Johnson, W. Chen, M.W. Wong, J.L. Andres, M. Head-Gordon, E.S. Replogle, J.A. Pople, Gaussian, Inc., Pittsburgh, PA, 1998.

[6] A. Yu. Kobitski, R. Scholz, D.R.T. Zahn, J. Mol. Struct. (THEOCHEM), submitted for publication.