THIN PENTACENE LAYER UNDER PRESSURE

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1. Introduction

Organic semiconductors have got a lot of interest during the last years, due to their usability for organic thin film transistor. Pentacene, $C_{22}H_{14}$, is one of leading candidates for this purpose [1]. It crystallizes in crystalline phases characterized by their *d (001)*-spacing of 1.41- 1.54 nm [2]. These phases can be identified by X-ray diffraction XRD [2] and Raman spectroscopy techniques [3, 4]. While we obtain the published data about pressure-induced phase transition only on single crystal of pentacene [4] we present pressure-induced phase transition in pentacene thin layers for the first time. Changes in the pentacene structure, caused by the pressure, were detected by micro-Raman spectroscopy.

2. Experimental details

A Jobin Yvon HR800 monochromator equipped with a CCD detector was used to record the micro-Raman spectra at room temperature in backscattering geometry. The micro-Raman spectra were excited with a He-Ne laser (633 nm line). The incident laser beam was focused by microscope lens to a spot size diameter of 1.3 μm.

For studying the pressure-induced phase transition of the thin pentacene layers we used heavily doped silicon wafers with a 40 nm thick thermally grown silicon dioxide insulating layer covered with parylene-C layer. Pentacene layers with a thickness of 70 - 130 nm were deposited on a top of the parylene-C layer by thermal evaporation at a pressure of 10^{-3} Pa at 30 and 70 °C with a deposition rate of 0.030 nm/s, monitored by a quartz crystal

detector. No further purification was performed for the commercially available pentacene material (Acros Organic).

Mechanical pressure to the pentacene layer was applied by the push of small iron ball (diameter ~ 6 mm) creating deformed area in pentacene of ~ 120 μm in diameter. In its centre greatly different Raman spectrum of pentacene was obtained. It is evidence, that in the centre the pentacene layer is fully destroyed. Beyond deformed area where the pentacene was not pressed measured Raman spectra are identical with those obtained from original virgin layer. Using experimental results published in [4] we have estimated pressure in the area with detectable Raman spectrum as high as 0.6 GPa. We were able to perform linear mapping across pressed area and to measure the Raman spectra as the function of increasing value of pressure.

3. Results and discussion

The linear micro-Raman mapping across pressed area in three positions are shown in Fig.1. In this figure we present the spectra in the region of 1140-1170 cm^{-1} where features of Raman spectra correspond to a motion of C-H atoms located at both ends of the pentacene molecules [5].

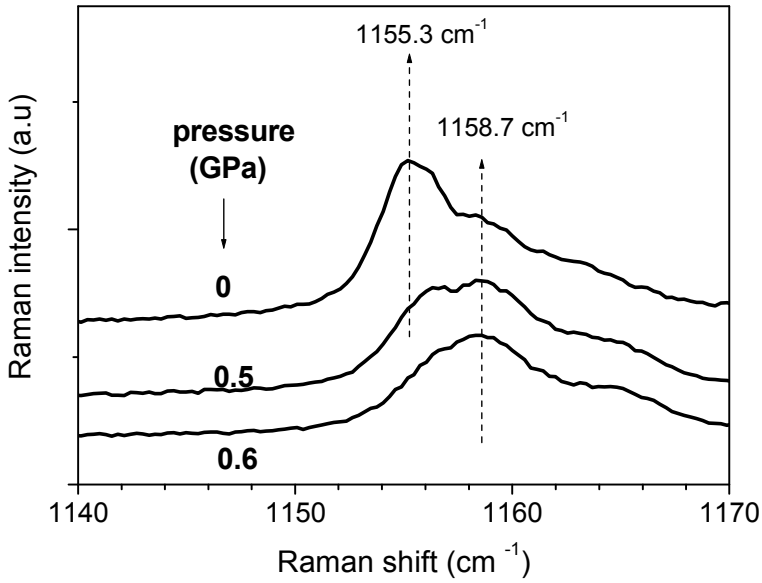

Fig.1*: Micro-Raman spectra of non-pressed pentacene and pressed by 0.5 and 0.6 GPa.*

The top spectrum corresponds to unpressed pentacene and bottom spectrum corresponds to the maximal applied pressure ~ 0.6 GPa. Spectrum in the middle corresponds to pressure of about 0.5 GPa. The blue shift in Raman spectra clearly indicates the

increasing pressure value. This dependence was obtained also at the pressure-induced phase-transition performed on single crystals of pentacene [4]. To the best of our knowledge, we have observed this dependence for the thin pentacene layer for the first time. In the Fig. 2a and 2b there are shown the measured and fitted Raman spectra without and with pressure. Lorentzian function was used for spectra fitting.

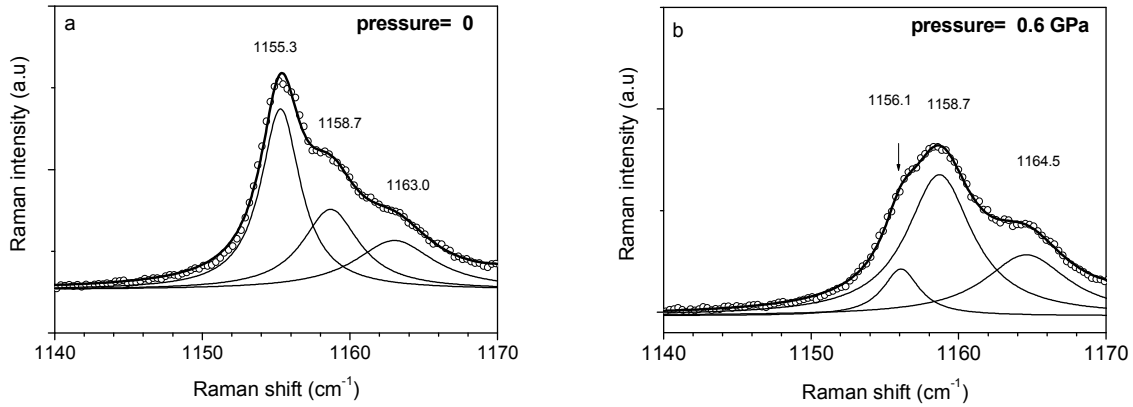

Fig.2: *Micro-Raman spectra of studied pentacene layer. a) no pressure b) at pressure of 0.6 GPa. Lorenzian function was used for fitting procedures (thin lines). Thick line represents resulting fitting dependence. Circles denote experimental data.*

The Raman spectrum of non-pressed pentacene layer (Fig.2a) shows the presence of pentacene good quality layer. The layer is composed mostly from thin phase: high intensity peak at 1155.3 cm^{-1}. Besides of thin phase there is present a smaller fraction of bulk phase presented by Raman peak at 1158.7 cm^{-1} [3]. XRD measurements confirmed these properties of studied pentacene layer (Fig.3).

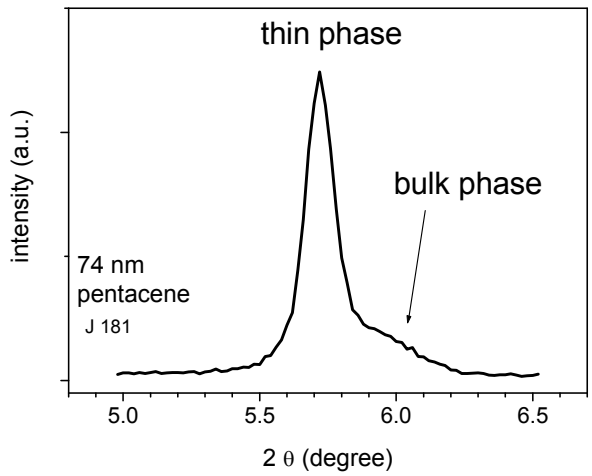

Fig.3: *XRD spectrum of studied pentacene layer. The high peak positioned at 5.7 ^{o} represents thin phase of pentacene. Bulk phase peak is broad and positioned at ~ 6.0 ^{o}.*

Using the pressure of 0.6 GPa the pentacene layer is transformed to the layer with high bulk phase concentration, represented by high intensity-peak positioned at 1158.7 cm^{-1} (Fig.2b), according to [3], while the thin phase peak (1155.3 cm^{-1}) disappeared. New peak with lower intensity, than bulk phase peak, positioned at 1156.1 cm^{-1} was detected. This means, that the molecules initially containing thin phase structure were transformed mostly to the bulk phase and with a smaller part to a non-identified phase under pressure. This unknown phase was also detectable by XRD in other works [6], but until now not fully described. We suppose, that by using the higher than 0.6 GPa all the pentacene molecules will be transformed to the bulk phase. Above described transformation from the thin to bulk phase was detectable also after some days at the same measurement conditions. Therefore we can declare that pressure-induced transformation is irreversible and can be detected by Raman spectroscopy.

4. Conclusion

Applying the defined pressure to the pentacene layer it can be transformed from thin phase to bulk phase. Micro-Raman spectroscopy was found as useful method for detection of changes and phases identification in the pentacene layer induced by mechanical pressure. Such a pressure-induced transformation of pentacene thin layers was observed and identified for the first time.

Acknowledgement

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