Infrared Spectroscopy of Bis(4-nitrophenyl) Disulfide Grown on a Pb Layer

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Crystal whiskers of bis(4-nitrophenyl) disulfide have been grown on a 100-nm thick Pb film from a supersaturated solution of *p*-nitrothiophenol. The whiskers preferentially grow on Pb but not on Si, In, or Ag. The crystals were characterized by electron microscopy and infrared spectroscopy. The optimized structure of the molecule was determined by ab initio calculations.

Surface-enhanced infrared absorption (SEIRA) is a phenomenon where the infrared (IR) absorption of molecules is enhanced by the presence of a metal surface.[1] *P*-nitrobenzoic acid (*p*-NBA) and *p*-nitrothiophenol (*p*-NTP) are common examples of molecules that exhibit SEIRA. Although Ag and Au are generally used as metals in these studies, recently it was reported that *p*-NBA on Pb showed evidence of SEIRA that depended strongly on the thickness of the Pb film.[2]

In this letter, we present the results of the growth and characterization of crystals grown from a *p*-NTP solution on Pb films. Unlike Ag or Au layers, self-assembled monolayers were not observed on thin (10 nm) Pb layers. On 100-nm thick Pb layers, however, we obtained evidence for the growth of bis(4-nitrophenyl) disulfide (NPD) crystals. Scanning electron microscopy (SEM) revealed that the crystals were present in the form of crystal whiskers a few microns in diameter and tens or hundreds of microns long. The IR transmission spectra of these whiskers are in good agreement with the published spectrum for NPD. In our experiments, no direct evidence for surface enhancement was found, perhaps due to oxidation of the Pb surface. Instead, the larger IR absorption on the 100-nm thick Pb layer as compared to the 10-nm layer was due to the fact that large crystals simply did not grow on the thin layer. The thin layer likely consisted of Pb islands, surrounded by Si which inhibited the growth of large NPD crystals.

Pb films were deposited on (100) Si substrates in a Perkin-Elmer ion-pump vacuum deposition system at a pressure of 10^{-7} Torr. No steps were taken to remove the oxide layer from the Si. A quartz gauge was used to monitor the Pb thickness during the deposition. NPD crystals were grown, at room temperature, from a supersaturated solution of *p*-NTP in methanol. It was found that NPD crystals did not grow on bare Si. When Si coated with a 100-nm layer of Pb was placed in the solution, however, the crystals grew within a few minutes. The crystals were yellow in appearance, and only weakly adhered to the Pb layer. To analyze the crystal morphology, we used a JEOL 6400 SEM with a 20 keV electron beam. The IR spectrum was obtained at room temperature with a Bomem DA8 Fourier transform infrared (FTIR) spectrometer with a KBr beamsplitter and mercury-cadmium-telluride (MCT) detector. The spectral resolution was $2\,\mathrm{cm}^{-1}$.

An SEM micrograph of the NPD crystals is shown in Figure 1. It can be seen that the crystal whiskers are approximately 3 microns wide and 30–100 microns long. The micrograph was taken near the edge of the Pb film. The dark region, where no crystals grew, is bare Si. This fact was verified by energy dispersive X-ray (EDX) analysis, which showed no Pb signal in the dark region. It is therefore apparent that the crystal whiskers grow preferentially on Pb but not on Si. Other experiments were performed with 100-nm layers of Ag and In, but crystals did not grow on those metals.

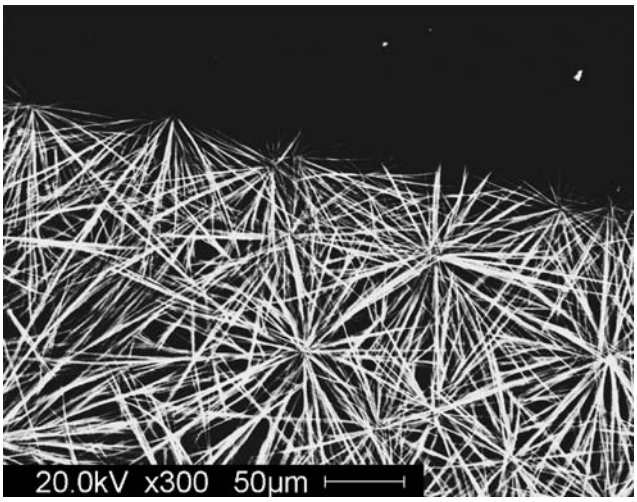

Figure 1. SEM micrograph of NPD grown on a Pb/Si substrate. The dark region, where no crystals grew, is bare Si.

An IR absorbance spectrum of the NPD sample is shown in Figure 2. A bare Si substrate, with neither Pb nor NPD, was used as the reference. The absence of a S–H mode at $2549\,\mathrm{cm}^{-1}$ indicates that the crystals are not *p*-NTP. Merklin et al.[3] found a

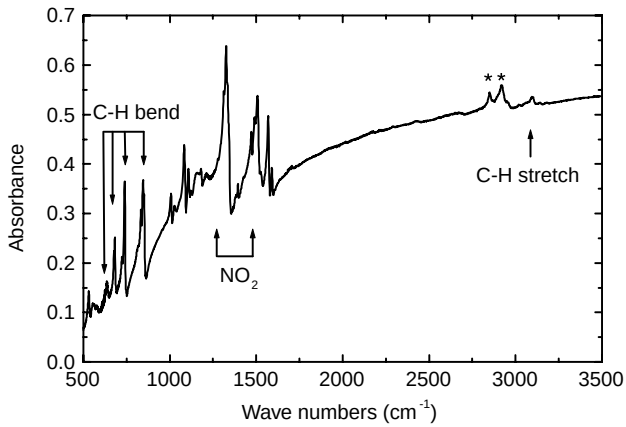

Figure 2. IR spectrum of NPD grown on a Pb/Si substrate. Peaks indicated by asterisks (∗) are due to the instrumental background. C–H and NO_2 modes arising from the NPD molecules are indicated by arrows.

similar result for NPD films that were cast from a solution of *p*-NTP. As in that work, our IR spectrum is in good agreement with the published spectrum for bis(4-nitrophenyl) disulfide.[4] The overall increase in absorption versus wave numbers may be a result of absorption by the Pb layer.

Ab initio calculations were performed in order to determine the structure of NPD molecules, using density functional theory (DFT).[5] We used the basis sets 6-311G(d) and 6-311++G(d). The larger basis set, 6-311++G(d), resulted in a nearly identical structure as that obtained by the 6-311G(d) basis set. The optimized structure for the NPD molecules is shown in Figure 3. This skewed structure is similar to that found for numerous disulfides.[6] The two phenyl rings are connected by the S–S bond, with a C–S–S–C dihedral angle of 81°. The NO_2 groups are rotated out of the plane of the phenyl rings by 33°.

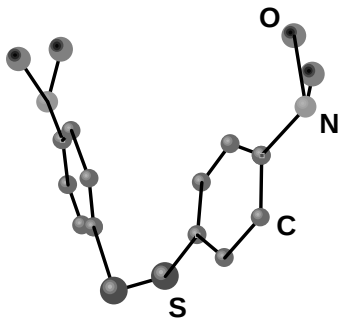

Figure 3. Calculated structure of the NPD molecule. Hydrogen atoms are not shown.

IR-active vibrational frequencies were calculated in the harmonic approximation. Modes involving significant motion of the S atoms were below 500 cm^{-1}, outside the spectral range of our measurements. Strong IR peaks arising from C–H bending modes were calculated at 679, 710, 745, and 860 cm^{-1}, in good agreement with the experimentally observed peaks at 637, 682, 739, and 845 cm^{-1}. Calculated C–H stretch modes were centered around 3200 cm^{-1}, in reasonable agreement with the observed peak at 3098 cm^{-1}. However, the calculated NO_2 IR peaks were 869 and 1154 cm^{-1}, significantly lower than the observed frequencies of 1326 and 1507 cm^{-1}.

In summary, NPD crystals have been characterized by SEM and IR spectroscopy. The growth of NPD crystals has been found to be strongly dependent on the substrate. This highly selective growth process may be useful for the fabrication of devices based on molecular crystals on Si.

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References

1 A. Hartstein, J. R. Kirtley, and J. C. Tsang, *Phys. Rev. Lett.*, **45**, 201 (1980).
2 T. Yoshidome, T. Inoue, and S. Kamata, *Chem. Lett.*, **1997**, 533.
3 G. T. Merklin, L.-T. He, and P. R. Griffiths, *Appl. Spectrosc.*, **53**, 1448 (1999).
4 "The Aldrich Library of FT-IR Spectra," 2nd ed., Sigma-Aldrich Co. (1997), Vol. 2, p 2340.
5 M. J. Frisch et al., "Gaussian 98, Revision A.9," Gaussian, Inc., Pittsburgh, Pennsylvania (1998).
6 T. Shimizu, H. Isono, M. Yasui, F. Iwasaki, and N. Kamigata, *Org. Lett.*, **3**, 3639 (2001), and references therein.