

Roughness-induced Raman scattering from surface carbon on PbTe

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(Received 20 December 1982)

Surface-roughness features on the scale of 0.1–0.3 μm induce enhanced Raman scattering from adsorbed amorphous carbon on PbTe. Analogous to the scattering by adsorbates on metal surfaces, the spectra show a strong continuum extending beyond 3000 cm^{-1} and no significant polarization dependence. The wavelength dependence of the enhancement exhibits a correlation with the band-structure properties of PbTe. These results are considered an indication that the scattering is due to roughness-induced coupling of the photons to nonvertical interband transitions at the surface. We discuss a possible explanation of the data in terms of a scattering mechanism which relies on the electrostatic interaction between electronic excitations of the substrate and the vibrational modes of the adsorbate.

Surface-enhanced Raman scattering (SERS) by molecules adsorbed on metal substrates has attracted considerable experimental and theoretical interest in the past few years.^{1,2} Although there has been some controversy in the literature, it is now generally believed that several mechanisms contribute to the enhancement.^{2,3} In this work, we report the first observation of this effect for a *nonmetal* substrate. Our results show that SERS in PbTe exhibits most of the features that are known to characterize SERS in metals, an indication that mechanisms which do not rely on specific properties of the latter materials could also be involved in an interpretation of this phenomenon.

Samples of single-crystal PbTe were grown by molecular-beam epitaxy on (111) BaF₂. Details concerning sample preparation and characterization procedures have been published elsewhere.⁴ Film thicknesses range from 1 to 3 μm . Raman data were obtained from more than 20 undoped, *n*-type (Bi-doped), and *p*-type (Tl-doped) samples, but no correlation with the nature or level of the doping was found. Samples with different surface morphologies were obtained by varying the temperature of the BaF₂ substrate during growth. Figure 1 shows electron micrographs of two distinct surface structures considered in this Communication. The surface of type-I samples, grown at $\sim 400^\circ\text{C}$, is smooth on the scale $\geq 300\text{ \AA}$. Type-II samples ($\sim 250^\circ\text{C}$ substrate temperature) exhibit an irregular array of triangular pits ($\sim 0.1\text{ }\mu\text{m}$ size, average separation $\sim 0.25\text{ }\mu\text{m}$), undoubtedly a remnant of their registration with the BaF₂ substrate.

Raman spectra were obtained with the samples in

10^{-6} Torr vacuum in the backscattering geometry, focusing the beam with a cylindrical lens to avoid excessive laser heating. Typical laser powers were 30–50 mW. The discrete visible lines of a Kr⁺ laser were used to determine the scattering intensities in the range 1.83–2.60 eV. Prior to the Raman measurements, the samples were etched in a solution consisting of 10 parts saturated KOH, 10 parts ethylene glycol, and 0.3 parts hydrogen peroxide at 0°C (this step was found to be crucial to assure reproducibility). The solution is known to etch PbTe at a rate of $\sim 40\text{ \AA/s}$.⁵ After immersion in the etchant for 10–15 s, the samples were quenched in ethanol,

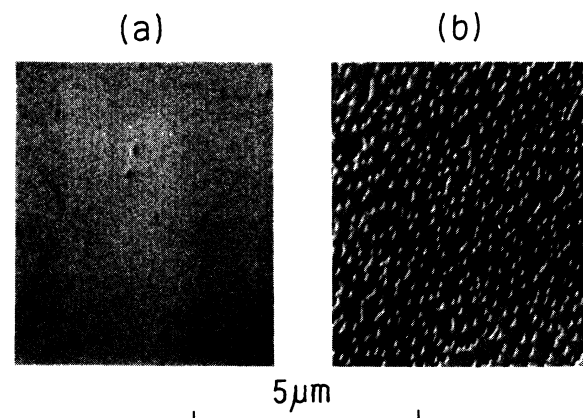


FIG. 1. Electron micrographs of (a) type-I and (b) type-II PbTe samples, grown on (111) BaF₂. Substrate temperatures during growth are (a) 400°C and (b) 250°C .

rinsed in distilled water, and dried in N_2 gas. Depth profile (argon sputtering) Auger measurements indicate that this procedure leads to the formation of a ~ 20 - \AA -thick surface layer (for both type-I and -II samples) consisting of carbon and Pb and Te oxides. Minor amounts of Cl were also found (< 1 at. %). The amount of carbon in the layers varied from 20 at. % to 40 at. % for different samples, irrespective of the surface morphology. Furthermore, Auger data obtained after sputtering ~ 50 \AA with the argon beam at an angle of $\sim 20^\circ$ above the surface exhibit no traces of carbon, indicating that the pits in type-II samples do not act as carbon sinks (a possibility that could have led to an underestimation of the total amount of carbon present in those samples). After being etched, the samples were transferred into the vacuum system. No special precautions were taken to prevent short contacts of the prepared surfaces with the air as the Auger data show that the carbon coverage increases only slowly as a function of time under these conditions (samples held in ambient pressure for a month exhibit a ~ 60 - \AA -thick surface layer with ~ 40 at. % carbon).

The Raman results are summarized in Fig. 2. The upper curve shows data typical of type-II samples. The spectrum is unpolarized and dominated by a broad, featureless band extending from 700 to 2200 cm^{-1} on top of a continuum background. The lower trace in the figure is the spectrum of type-I samples obtained under similar conditions and plotted on the same scale. The broad band and the continuum, as seen in a smaller scale, show a dramatic decrease in intensity by a factor of ~ 100 . We show below that the broad structure is due to scattering from carbon on the PbTe surface. Based on the fact that the total amount of carbon in type-I and -II samples is approximately the same (1–2 equivalent monolayers), we attribute the enhanced scattering in the latter samples

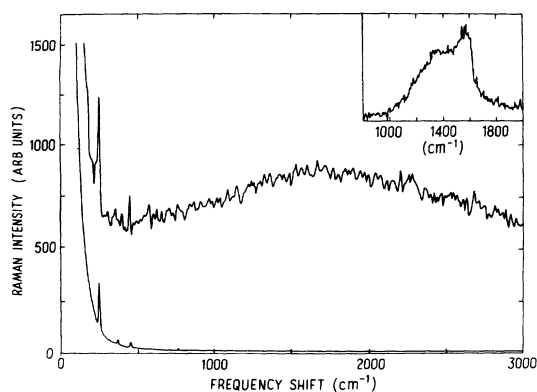


FIG. 2. Raman spectra from 1–2 monolayers of carbon (see discussion in the text) on type-I (lower curve) and type-II (upper curve) PbTe surfaces. The inset shows the spectrum of a type-II sample after annealing ~ 12 h at 200°C .

to the presence of the array of pits. A crude estimate of the absolute value of the enhancement was made by comparing the integrated intensity in the spectrum of the type-II sample to that of the E_g mode of graphite at 1582 cm^{-1} . Assuming the same bond polarizability, we find an enhancement factor of 0.5 – 1×10^3 , an indication that the scattering from type-I samples may also be (weakly) enhanced.

The assignment of the band in Fig. 2 to Raman scattering from carbon is based on the similarity with the spectrum of amorphous carbon⁶ which shows a ~ 400 - cm^{-1} -broad peak with maximum at 1550 cm^{-1} .⁷ Annealing studies done on our samples at 200°C and 10^{-6} Torr vacuum indicate that the band gradually narrows as a function of time and eventually develops a double peak structure, as shown in the inset of Fig. 2. The two peaks at 1360 and 1590 cm^{-1} have often been found in SERS studies on metals^{8–11} and ascribed to the presence of graphitic carbon on the surface.⁹ It is not clear why the carbon peak in our samples is far broader (factor of ~ 3) than what is found in bulk amorphous carbon. However, it is most probably related to large fluctuations in the C–C bond length that are suppressed by the annealing.

As in SERS from metals, our data also show the presence of a continuum extending beyond 3000 cm^{-1} . Different interpretations have been proposed for the origin of the continuum in the case of metals involving the vibrational modes of the adsorbate,¹² surface plasmon polaritons,¹³ and electron-hole pair excitations.¹⁴ Surface plasmons in PbTe are heavily damped (see below) and, therefore, unlikely to couple effectively to the light. Scattering associated with the recombination of electron-hole pairs cannot explain our results because such excitations should exhibit a low-energy cutoff at the position of the band gap of PbTe (~ 1500 cm^{-1}) which is not apparent from the data.¹⁵ We believe that the continuum here originates from electronic excitations and/or vibrational modes intrinsic to adsorbed carbon. In this respect, it is important to point out the similarities with the Raman data of some intercalate-graphite compounds, for which the origin of the continuum is still the source of much controversy.¹⁶

The relative magnitude of the enhancement was determined for five discrete lines of a Kr^+ laser at $\omega = 1.83, 1.91, 2.33, 2.38,$ and 2.60 eV, after correcting for the system response. The intensity of the carbon band is approximately the same for the green-blue lines, but a factor of ~ 200 larger than in the red. There are different possible interpretations of this behavior which relate to different models of SERS.³ First, the real part of $\epsilon(\omega)$ for PbTe changes from being positive in the red to negative values at ~ 2.1 eV, and remains negative up to $\omega \sim 5.5$ eV.¹⁷ This fact and the energy dependence of the scattering might suggest the involvement of electromagnetic

resonances of the roughness features as the cause of the enhancement.^{2,3} These resonances are known to play an important role in SERS from metals.^{2,3} A problem with this interpretation is that the resonances are clearly too broad in PbTe [the imaginary part of $\epsilon(\omega) \sim 15-20$ in the visible¹⁷] to account for the factor of ~ 200 difference between the red and green-blue regions. We have calculated the response function for surface plasmons at different wave vectors and found that it varies at most by a factor of ~ 2 in the range of interest. An additional point against the participation of surface plasmons in the scattering process is that the scale of roughness in our samples should lead to photon-plasmon coupling at $\omega \approx 4-5$ eV, i.e., far away from the range studied. Mie-type resonances associated with the pits are also expected to be heavily damped partly due to the large values of $\text{Im}[\epsilon(\omega)]$, but also because $2\pi\delta/\lambda \approx 1$ (δ is a characteristic size of the pits).

A more likely explanation of our results is that the relevant intermediate states in the Raman process involve interband transitions in PbTe (which can be nonvertical due to the presence of roughness). This is suggested by the fact that the range where we find the large enhancement correlates with the position of a number of critical points in the joint density of states of PbTe (Ref. 17) (the onset of transitions among bands in the Σ and Δ directions are at $\omega \sim 2.1-2.3$ eV). Furthermore, no critical points occur for $1.25 < \omega < 2$ eV (Ref. 17), a region which includes the laser lines for which the large decrease in the enhancement is observed.

To understand the role played by the roughness, we consider the Fourier transform of the Coulomb interaction between an electron (or a hole) confined in the substrate and the dipole moment $\vec{\mu}$ associated with a vibrational mode of the adsorbate (this analysis assumes that the modes that scatter are also infrared active, a condition that applies to amorphous carbon due to the lack of symmetry constraints). Various models of SERS have already referred to this interaction as the source of scattering in the case of

metal substrates.^{18,19} The Hamiltonian

$$H_{\vec{k}} = \frac{8i\pi e}{(\epsilon_0 + 1)V} \frac{\vec{\mu} \cdot \vec{k}}{k^2} \exp[i\vec{k} \cdot (\vec{r}_e - \vec{r}_\mu)] \quad (1)$$

where \vec{r}_e , \vec{r}_μ are the position vectors of the electron and molecule, V the sample volume, and ϵ_0 the low-frequency dielectric constant of the substrate, gives rise to transitions between electronic states at \vec{q}_1, \vec{q}_2 such that $(\vec{q}_1 - \vec{q}_2) = \vec{k}$, while promoting the oscillator to a higher (or lower) quantum state. For a smooth surface, $|\vec{k}| \approx k_0 \ll \pi/a_0$ (k_0 is the wave vector of the photons and a_0 is the lattice parameter) and the Raman matrix vanishes due to the cancellation of the electron and hole contributions.²⁰ In the presence of roughness $\vec{k} \approx 2\pi n\hat{j}/l$, \hat{j} is a unit vector parallel to the surface, and l is a roughness length ($l \approx 2500$ Å in type-II samples). Cancellation does not happen in this case provided a_0/l is not too small. Even if $a_0/l \ll 1$, the electron and hole contributions will not cancel out when the roughness is random, due to the *lack of coherence* between the two terms. This situation is likely to lead to a large enhancement factor because of the k^{-1} divergency in Eq. (1) and is consistent with our scale of roughness. For the mechanism to be operative, it is required that most of the power be coupled to electronic excitations near the surface as indicated by the exponential factor in the Hamiltonian. The penetration depth of visible light in PbTe is of the order of ~ 200 Å. This is close to values found in noble metals.

In summary, we have shown that a nonmetal substrate can also exhibit SERS with properties similar to those of metals, and we have discussed a possible explanation of the data which stresses the effect of roughness on the coherence of the electron and hole contributions to the scattering matrix.

This work was supported in part by the U.S. Army Research Office under Contract No. DAAG-29-82-K0057, and Research Corporation.

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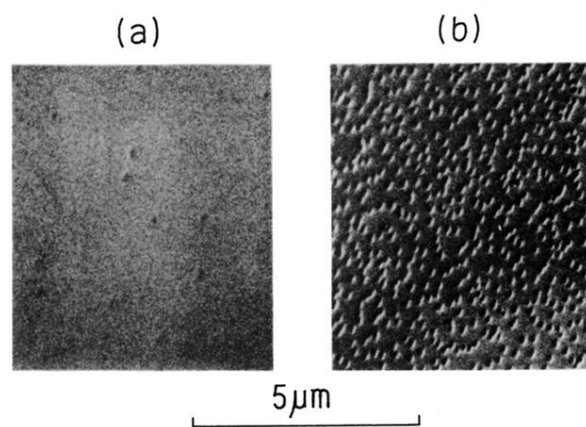


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