Raman scattering in carbon films at high pressures

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The Raman spectra of diamondlike and graphitelike thin carbon films obtained by deposition from the gas phase were measured at high pressures (up to 80 and 48 GPa, respectively). We observed stability of the structure of the diamondlike film over the entire pressure range studied and the transformation of the graphitelike film at 44 GPa to a different modification—a transformation analogous to that observed earlier in glassy carbon and pyrographite. The observed baric shifts of the Raman bands are correlated with available data for graphite and diamond.

INTRODUCTION

In the last few years, preparation of various coatings of atomic carbon has become one of the rapidly progressing trends in technology.[1] An ideal method for the diagnostics of these items is the method of Raman spectroscopy, which permits an effective determination of the phase composition of the films. As is well known, the most common modifications of atomic carbon are diamond and graphite, the Raman spectrum of each of which shows the predominance of a single strong band (1332 cm^{-1} and 1580 cm^{-1}, respectively). When carbon films are deposited, depending on the conditions of deposition, the material, and the orientation of the substrate, formation of coatings of different characteristics, usually with an amorphous or finely crystalline structure, is possible. One of the most typical coatings is a film of amorphous graphitelike *i*-C carbon (glassy carbon), which essentially is a highly disordered graphite having crystallites ~ 1 nm in size. The Raman spectrum of this carbon modification is very weak and represented by two bands, 1350 cm^{-1} and 1600 cm^{-1}. The higher-frequency band corresponds to the graphite line, and the low-frequency band, arising in disordered graphite structures, is usually attributed to the density peak of the phonon states near the edge of the Brillouin zone. Another modification of carbon films consists of so-called diamondlike films of amorphous carbon (*a*-C). Diamondlike films are characterized by a much more intense Raman spectrum, in which the broad 1550-cm^{-1} band with a shoulder at 1340 cm^{-1} is predominant. According to the data of Ref. 2, the strength ratio of these bands makes it possible to estimate the relative content of sp^2 and sp^3 bonds in an *a*-C film.

In the present work, Raman spectra of diamondlike and graphitelike thin films at ultrahigh pressures have been studied for the first time. The baric shifts of the observed Raman bands were determined; it was found possible to correlate them with the corresponding shifts in graphite and diamond single crystals. We observed the transition of a graphitelike film to an amorphous structure analogous in its spectra to a diamondlike film.

EXPERIMENT

The technique of a Raman experiment at high pressures and room temperature using diamond anvils was described in Ref. 3. As in the experiments of Refs. 3 and 4, the medium transmitting the pressure was compressed helium. The pressure in the chamber was determined with the aid of a ruby luminescence manometer.[5] Carbon films of different phase compositions were deposited from a gas-discharge plasma by use of the method described in Ref. 6, and after removal from the substrate, they were stacked in a high-pressure chamber. The x-ray diffraction data and their detailed analysis based on *i*-C and *a*-C films are presented in Refs. 6–8.

RESULTS AND DISCUSSION

Transition from the graphitelike to the diamondlike state. Figure 1 shows the Raman spectra of graphitelike thin films of *i*-C at different pressures. In the 40–43 GPa range, an abrupt change in shape of the Raman spectra takes place. Instead of two bands, characteristic of the disordered graphite phase, one broad asymmetric band appears, and the spectrum becomes analogous to that of the diamondlike film (*a*-C) at the same pressures (see Fig. 2). An analogous transformation of the spectra was observed in glassy carbon and pyrolytic graphite.[4] For $P > 40$ GPa, the pressure dependence of the fundamental-band maximum (see Fig. 3) levels off as in the case of single-crystal graphite,[4] indicating the formation of an instability of the planar carbon layers. When the pressure is relieved, the resulting state of the carbon is found to be stable up to ≈ 20 GPa, and the dependence $\nu(P)$ follows the corresponding dependence for *a*-C (see below), and this is followed by relaxation to the graphitelike phase with the characteristic spectrum of the *i*-C film. Thus, an appreciable hysteresis of the transformation is observed.

Behavior of the diamondlike film. In contrast to the *i*-C film, the Raman spectra of the *a*-C diamondlike film do not undergo any appreciable changes under the action of pressure. One observes only a regular baric shift of the Raman bands, a shift that can be correlated with analogous shifts observed in graphite and diamond (see below). We also note that the Raman spectrum of the diamondlike film is approximately an order of magnitude more intense than the spectrum of the high-pressure phase, although it is very similar in shape. The above facts evidently indicate that the structure of the high-pressure phase is not completely analogous to the *a*-C phase and most probably constitutes a distorted graphite structure in which crimping of the layers has taken place along with a partial transition of the carbon atoms from the sp^2 to the sp^3 state, but without any new bonds being formed; this promotes relaxation of this structure to the initial one when the pressure is relieved. On the contrary, the *a*-C phase

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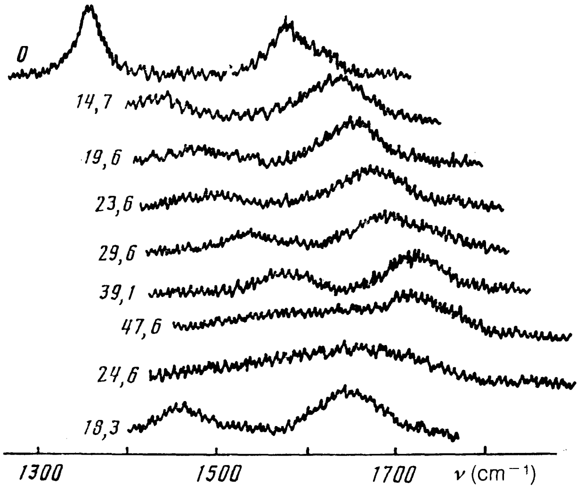

FIG. 1. Raman spectra of *i*-C film at different pressures (numbers next to the spectra represent values of pressure in GPa).

is a hardened structure with a mixed system of sp^2 and sp^3 bonds which do not break in the pressure range studied. At the same time, there is a definite tendency for the frequencies of the corresponding bands at high pressures to come closer together, which evidently indicates a gradual transformation of the structure to a state with the same bond type.

Dependence of the frequencies of the vibrational modes on pressure. Figure 3 shows curves of the Raman band frequencies of the *i*-C (1360 cm^{-1} and 1580 cm^{-1}) and *a*-C (1340 cm^{-1} and 1550 cm^{-1}) films. The baric shifts of the Raman bands were analyzed by means of the relation

$$P=A(\nu/\nu_0-1)+B(\nu/\nu_0-1)^2, \qquad (1)$$

where ν and ν_0 are, respectively, the running and initial values of the frequency, and A and B are coefficients determined by the method of least squares.

For the *i*-C film (pressure range up to 40 GPa), we obtain

$$\nu=(1360\pm5)\text{cm}^{-1},\ A=(218\pm8)\ \text{GPa},\ B=(260\pm67)\ \text{GPa},$$
$$\nu=(1580\pm2)\text{cm}^{-1},\ A=(364\pm20)\ \text{GPa},\ B=(530\pm270)\ \text{GPa}, \qquad (2)$$

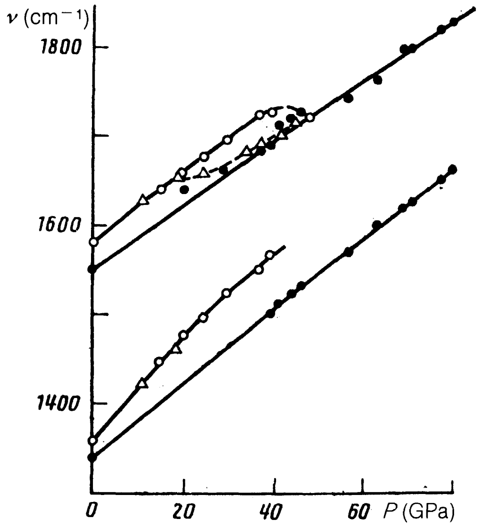

FIG. 3. Raman band frequencies of carbon films vs pressure: ●—*a*-C; ○—*i*-C (pressure increases); △—*i*-C (pressure decreases). Solid lines—MLS calculation (see text); the dashed line was drawn freehand for the *i*-C film after transition to a state analogous to *a*-C.

and for the *a*-C film

$$\nu=(1340\pm5)\text{cm}^{-1},\ A=(313\pm7)\ \text{GPa},\ B=(95\pm33)\ \text{GPa},$$
$$\nu=(1550\pm5)\text{cm}^{-1},\ A=(383\pm24)\ \text{GPa},\ B=(380\pm170)\ \text{GPa}. \qquad (3)$$

The coefficient A is related to the Grüneisen mode parameter simply as follows:

$$\gamma_i=K/A_i, \qquad (4)$$

where K is the modulus of bulk elasticity.

In general, Eq. (4) holds for isotropic substances with a single type of interatomic bonds. For anisotropic substances and/or substances with different interatomic interactions, it is helpful to consider microscopic Grüneisen mode parameters γ_0, which relate the changes in frequencies to the changes in bond lengths:[9]

$$\nu/\nu_0=(r/r_0)^{-3\gamma_0}.$$

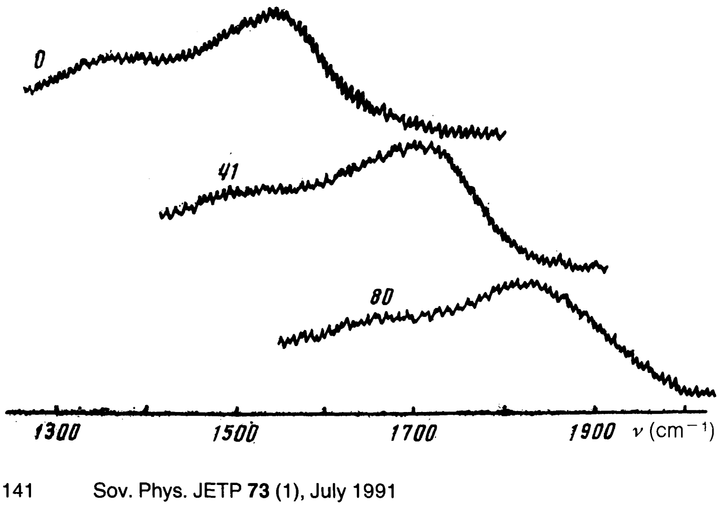

FIG. 2. Raman spectra of *a*-C film at different pressures.

For an anisotropic substance such as graphite (as well as the *i*-C film),

$$\gamma_0=(3\beta\nu_0)^{-1}(d\nu/dP), \qquad (5)$$

where $\beta^{-1} = 1250$ GPa,[10] and β is the linear compressibility of C—C bonds in hexagonal graphite layers. From Eqs. (1), (2), and (4), we find for the *i*-C film

$$\nu=1360\,\mathrm{cm}^{-1},\ \gamma_{01}=1{,}91\pm0{,}08,$$
$$\nu=1580\,\mathrm{cm}^{-1},\ \gamma_{02}=1{,}15\pm0{,}06.$$

We note that the value of γ_{01} shows excellent agreement with the value $\gamma_{11} = (1.99 \pm 0.09)$, which can be obtained from an analysis, analogous to the one given here, of data on second-order Raman scattering in single-crystal graphite for the band $\nu_{11} = 2720\ \mathrm{cm}^{-1}$.[3] This fact confirms the validity of assigning the 1360 cm^{-1} band [the maximum of the density function of phonon states, which arises from the leveling off of the dispersion curves at the edge of the Brillouin zone near the points *M* and *K* (Ref. 11)] and its overtone coupling to the 2720 cm^{-1} second-order band. In this coupling, the disappearance of the 1360-cm^{-1} band at $P > 40$ GPa is easily explained by the breakdown of periodicity within the crystallites comprising the *i*-C film during the transition to the amorphous state.[4]

In analyzing the data for the diamondlike film, we use the concept of the *a*-C structure as a mixture of graphitelike and diamondlike bonds with a $\approx 15\%$ content of the latter.[12] In this case, the formulas obtained by Zallen[9] for substances with different types of interactions are modified to the following form:

$$\gamma_{gr0}=\gamma_{gr}(1+n\alpha)(1+nm^{-1})^{-1},$$
$$\gamma_{di0}=\gamma_{di}(1+n^{-1}\alpha^{-1})(1+n^{-1}m)^{-1}, \qquad (6)$$

where the indices *gr* and *di* pertain to graphitelike and diamondlike bonds, respectively, $n \approx 0.15$ is the relative content of diamondlike bonds in *a*-C, $m = (r_{gr}/r_{di}) \approx 0.92$, and $\alpha = (k_{gr}/k_{di}) \approx (\nu_{gr}/\nu_{di})^2 \approx 1.34$ is the ratio of the corresponding force constants. The Grüneisen mode parameters γ_{gr} and γ_{di} can be obtained from Eq. (4) by means of the experimental data (3). Assuming that the modulus of bulk elasticity for *a*-C is determined by the dominant graphitelike bonds, we obtain

$$\gamma_{gr}=1{,}09\pm0{,}05,\ \gamma_{di}=1{,}33\pm0{,}03. \qquad (7)$$

At the same time, calculation of the microscopic Grüneisen parameters for C—C bonds (6) gives

$$\gamma_{gr0}=1{,}13,\ \gamma_{di0}=1{,}11,$$

i.e., $\gamma_{gr0} \approx \gamma_{di0}$. The values obtained agree fairly well with the Grüneisen parameters of the corresponding modes in graphite [$\gamma = 1.06$ (Ref. 10); analysis of the data of Ref. 3 allowing for $\beta^{-1} = 1250$ GPa gives $\gamma = 1.11 \pm 0.03$] and in diamond[13] ($\gamma = 0.96$). Thus, allowing for the difference in interatomic interactions makes it possible to explain the baric shifts observed.

CONCLUSIONS

The measurements confirmed the previous assignment of the Raman bands in the *i*-C and *a*-C carbon films. It was found that although the frequencies of the 1340-cm^{-1} band in *a*-C and 1360-cm^{-1} band in *i*-C are very similar, their nature is different. The former is related to diamondlike bonds, and the latter arises from the disorder of the crystal structure of the *i*-C film because of the breakdown of the selection rules. It was also found that despite the similarity of the Raman spectra of the *a*-C film and high-pressure phase formed from *i*-C at high pressures, their structures are different. The latter structure most probably is a distorted structure of graphite and relaxes to the graphite structure when the pressure is removed.

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