Synthesis and characterization of cluster-assembled carbon thin films

P. Milani,^{a)} M. Ferretti, and P. Piseri INFM-Dipartimento di Fisica, Università di Milano, via Celoria 16, 20133 Milano-Italy

C. E. Bottani, A. Ferrari, and A. Li Bassi INFM-Dipartimento di Ingegneria Nucleare (CESNEF), Politecnico di Milano, via Ponzio 34/3, 20133 Milano-Italy

G. Guizzetti and M. Patrini INFM-Dipartimento di Fisica "A. Volta," Università di Pavia, via Bassi 6, 27100 Pavia-Italy

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Nanostructured carbon thin films have been produced by deposition of supersonic cluster beams. The clusters are generated by a pulsed arc cluster ion source modified in order to achieve high fluxes and stability. Scanning electron microscopy, Raman, and optical spectroscopy show that the films are a low density network of nanometer-size particles. The nature of the films is essentially graphite-like with a large number of distorted bonds. The formation of structures based on sp^3 bondings is not observed. The use of cluster beam deposition for the synthesis of nanocrystalline thin films is discussed. © 1997 American Institute of Physics. [S0021-8979(97)07123-5]

I. INTRODUCTION

Nanostructured materials are subject of an increasing interest as a consequence of their peculiar structural, electronic, and mechanical properties.¹ This field of research can strongly benefit from the efforts devoted to the characterization of clusters and small aggregates. The physical and chemical properties of these objects are size specific so that they can be considered as building blocks for the synthesis of materials with tailored properties controlled by changing the size and composition of the primeval clusters.²

Among many methods of production of nanostructured materials,³ the assembling of clusters seems to be very versatile and promising, expecially for thin film synthesis. A necessary requisite for large scale and reliable use of this technique is the development of efficient production and characterization methods to control cluster nucleation, deposition, postdeposition coalescence etc, in order to correlate the final product with the precursors.

Several authors have proposed cluster beam deposition as a tool for the synthesis of nanostructured thin films:^{4–6} Clusters produced in the gas phase are accelerated in a supersonic beam and then deposited on a substrate. Compared to ion beam implantation the use of clusters offers new opportunities such as chemically activated reactions, shallow implantation,⁶ moreover the control of cluster mass distribution and cluster deposition energies can allow the growth of films with a tailored nanocrystalline structure.^{4,5}

The application of cluster beam deposition to the synthesis of nanocrystalline carbon thin films seems to be very attractive. The control of deposition energy and mass distribution should open the possibility of tuning the sp^2-sp^3 ratio of the film, moreover the introduction of fullerenic structures embedded in an amorphous matrix could influence the mechanical properties of the nanostructured materials.^{7,8}

Compared to the enormous amount of experimental and theoretical results on carbon films constructed. "atom by

atom,"⁹ the characterization of cluster-assembled carbon materials is still in its infancy. Theoretical researches on nanostructured and nanoporous materials have explored new classes of solids, based on the assembling of small carbon units.^{10,11} On the other hand, relatively few experimental efforts have been produced towards the synthesis and the characterization of these materials.

Recently nanocrystalline carbon films have been produced by depositing supersonic cluster beams generated by a laser vaporization source^{4,12} and by collecting on a substrate the particles produced in an arc-plasma apparatus.⁷ In both experiments, the deposition conditions were not systematically established. Moreover, recent numerical simulations of carbon cluster deposition raised some questions about the interpretation of the experimental results of film characterization and in particular on the formation of sp^3 networks from the assembling of small fullerenes.¹⁰

Here we present a characterization performed by scanning electron microscopy (SEM), Raman spectroscopy, optical reflectance, and ellipsometry of nanocrystalline carbon thin films deposited by cluster beams produced with a novel plasma cluster source. The analysis of carbon films shows that, in the deposition energy range used, they have a nanoporous structure with an essential sp^2 character of the bonds. We have also carefully characterized the source performance and the cluster beam prior to deposition. We show that this kind of source can be conveniently used for the deposition of thin films of refractory materials.

II. EXPERIMENTAL SETUP AND SAMPLE DEPOSITION

A schematic view of the deposition apparatus is shown in Fig. 1. A supersonic beam of clusters is produced by a modified version of a pulsed arc cluster ion source (PACIS).¹³ A carbon plasma is generated by an intense electrical discharge produced between two graphite rods. The plasma is mixed with a pulse of inert buffer gas (helium with a pulse width of several hundreds of microseconds) to favor thermalization and cluster aggregation; the mixture is then

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^{a)}Electronic mail: pmilani@mi.infn.it



FIG. 1. Schematic view (not to scale) of the experimental apparatus used for thin film deposition.

expanded into a vacuum. In order to improve the stability and the intensity of the source, we have introduced several modifications as compared to the original design.⁵ A detailed description of the source will be published elsewhere,¹⁴ here we only underline the introduction of a chamber¹⁵ where the plasma thermalizes before the expansion, drastically increases the stability, the mass range, and the intensity attainable, rendering this type of source very attractive for the deposition of nanostructured thin films of refractory materials.

The characterization of the different cluster mass distribution and charge states in the beam has been performed with a linear time-of-flight (TOF) mass spectrometer.¹⁶ Neutral clusters have been ionized with the fourth harmonic (266 nm) of a Nd: yttrium aluminum garnet (YAG) laser. Cluster fluxes have been characterized with a quartz microbalance and with a Faraday cup placed in the deposition chamber after the first skimmer (see Fig. 1). In Fig. 2, we show a mass spectrum of neutral clusters produced with source conditions



FIG. 2. Mass distribution of carbon clusters used as precursors of thin films. The TOF spectrum has been obtained by ionizing the clusters in the beam using the fourth harmonic (266 nm) of a Nd:YAG laser.

used for film depositions. The mass distribution is peaked around 500 atoms per cluster, with contributions from aggregates up to about 2500 atoms per cluster.

The center of mass of the size distribution and charge state are strongly influenced by the presence of the thermalization cavity. The clusters residence time depends on parameters such as the pressure reached in the cavity, its volume, and the conductance of the nozzle. The spectrum in Fig. 2 has been recorded with a delay time T_d between the arc discharge and the laser ionization of 1100 μ s. This delay is the convolution of the residence time of the cluster in the source with the time necessary for the cluster to reach the TOF mass spectrometer. Mass spectra have been recorded for a very wide range of T_d (several milliseconds), showing that the center of mass of the size distribution is influenced by the residence time. For very large T_d , clusters of several thousands of carbon atoms contributed to the mass spectra, however without changing substantially the position of the center of mass of the size distribution. The mass distribution of clusters ions (cations) is substantially different from that of neutrals: 0-1200 atoms/cluster (with mass distribution centered at 350 atoms/clusters) for ions, against 0-3000 atoms/cluster (centered at 750 atoms/cluster) for neutrals. This is probably due to a trade off between cluster growth and charge neutralization: the growth of large clusters requires long residence times inside the source, but this also implies a bigger chance to be neutralized. Our results suggest that the assumption frequently made on the correspondence of the neutral and ion cluster beam produced by the same source must always be carefully verified.⁴

By growth rate measurements, performed with the quartz microbalance, the overall beam intensity has been estimated to be in the range of $3 \times 10^{14} \approx 1 \times 10^{15} \text{ s}^{-1} \text{ sr}^{-1}$ particles, depending on the discharge voltage. A fraction of about 10% of the total average flux is due to anions, while cations are about 2%. Neutral cluster velocities are in the range of 1400–1800 m/s, depending on the exit time. The typical kinetic energy of a medium-size cluster is thus about 0.3 keV. The velocity of the cluster ions is spread over the range 1200–1900 m/s, with the distribution being peaked at 1700 m/s.

Thin film deposition has been performed by intersecting the cluster beam with the substrate placed on a three axis micromanipulator. The temperature of the substrate [Si(100)] can be controlled from 77 to 600 K. Films of thicknesses from 100 to 500 nm over an area of several square centimeters, have been grown under a vacuum of 10^{-7} Torr with deposition rates of 25 Å/min. Some of the deposited films have been annealed *in situ* at different temperatures.

Micrographs of the films were performed with a Cambridge Stereoscan 360 scanning electron microscope with a 5 kV SEM acceleration and a 150 pA probe current. Unpolarized Raman spectra were recorded *ex situ*, at room temperature in backscattering geometry, using an I.S.A. Jobin–Yvon triple-grating spectrometer with a liquid nitrogen cooled camera detection (CCD) system. The spectral resolution was about 3 cm⁻¹; the 514.5 nm line of an Ar ion laser was used as excitation source; power on the sample was about 3 mW.

Reflectance spectra at near normal incidence and at room temperature were measured by a spectrophotometer Varian mod. Cary 5E is utilized over the spectral range of 0.4–6 eV. An Al mirror, whose absolute reflectivity was previously and independently measured, was used as reference.

Ellipsometric functions tan ψ and $\cos \Delta$ were measured between 1.5 and 5 eV with a spectroscopic ellipsometer Sopra mod. Moss ES4G was equipped with a microspot system. The angle of incidence was 65°, close to the Brewster angle for optimum sensitivity. Spectral resolution was better than 4 meV over the whole spectral range. We recall that ellipsometry measures the complex ratio $\tilde{\rho}$ of the parallel to perpendicular polarization reflection coefficients, i.e., $\tilde{\rho} = \tilde{r}_s / \tilde{r}_p$ = tan $\psi e^{i\Delta}$. In order to determine the complex refractive index $\tilde{n} = n + ik$ of the film, where *n* is the usual refractive index and k is the extinction coefficient, we inverted the $\tan \psi$ and $\cos \Delta$ spectra employing a three-phase optical model (air-film substrate). The *n* and *k* values of silicon were taken from literature; the film thickness d was initially taken from SEM measurements and then adjusted to optimize the inversion algorithm.

III. RESULTS AND DISCUSSION

Figure 3(a) shows a low-magnification micrograph of a film deposited at room temperature. A section of the film is shown at different magnifications in Figs. 3(b) and 3(c). A spongelike structure is visible, formed by aggregates with dimensions ranging from several hundreds of nanometers down to 20 nm, randomly stacked. This visual inspection suggests a porous structure with a possible self-similar organization. The softness of the material¹⁷ prevented a detailed investigation of the morphology of the smallest grains since they vibrate under the high electron current necessary to obtain high magnification.

Figure 4 shows the Raman spectrum of a film deposited at room temperature. In the low frequency range, we observe a broad hump extending from roughly 650 to 800 cm⁻¹ and peaked at about 740 cm⁻¹.

The region between 1000 and 1800 cm^{-1} presents two resolved peaks at about 1584 and 1363 cm⁻¹, superimposed to a broad structure. The two peaks can be identified as the Gpeak of crystalline graphite arising from zone-center E_{2g} mode, and the D peak assigned to an A_{1g} zone-edge phonon activated by the disorder due to finite crystalline size.^{18,19} The Raman signal in this region can be fitted with four gaussians. If all 13 fitting parameters (12+background) are allowed to vary, the procedure is unstable and, in most cases, the outcome is the overlapping of gaussians in pairs, giving excellent fits but without any physical significance. The best solution is obtained fixing the shifts of two features at 1180 and 1490 cm⁻¹ and allowing all other unknowns to vary (Fig. 5). The above shifts were chosen because, when the unconstrained fit was not giving overlapping results, they produced two small features around those positions.

The region between 2000 and 3400 cm^{-1} is characterized by second order Raman scattering.¹⁸ The spectrum displays a faint bump around 2000 cm⁻¹ and a broad structured feature between 2200 and 3400 cm^{-1} , with a peak around 2700 cm⁻¹.



FIG. 3. SEM micrographs of a nanocrystalline carbon thin film. (a) Lowmagnification micrograph of the surface. (b) and (c) high magnification view of a section of the film: The granular structure is clearly visible. Grains as small as roughly 20 nm can be seen.

The interpretation of the Raman features can be related to the mass distribution of the precursors and the history of the precursors after the deposition. The degree of fragmentation and coalescence of the cluster will determine the final structure and morphology of the film. As a starting point, we can assume that our clusters substantially retain on the substrate of their individuality, due to the low energy deposition



FIG. 4. Raman spectrum of a film deposited at room temperature. The sharp peaks at 520 and 970 cm^{-1} are due to the silicon substrate.

(less than 1 eV per atom for medium size clusters). This suggests that the films should be composed of a random stacking of clusters eventually linked, as proposed in Refs. 4 and 12. Although the SEM analysis confirms the granular nature of the film and the presence of a "memory effect,"⁴ the observation of structures of several tens nanometer in diameter, suggests that the original clusters may strongly interact and coalesce. It should be reminded that several isomers are present in the cluster beam with different structures and reactivities.²⁰ Only particular fullerenes (C_{60} , C_{70}) have a high stability; other cage structures, especially in excited states, are fragile and they can react to each other. The coexistence of different types of clusters in the beam can account for the formation of a low density material composed by primeval carbon clusters embedded in a connecting medium formed by the coalescence of small fragments and/or defected large clusters. Moreover, in our case, due to the cluster mass range used for deposition, it is reasonable to expect a film with a sp^2 character, with the presence of deformed rings and only a small number of sp^3 bonds.

The predominant sp^2 character of the film is confirmed by Raman spectra. The overall spectra, and in particular the intensities and the shapes of G and D bands are typical of



FIG. 5. Raman spectrum in the region between 1000 and 2000 cm^{-1} which is expected to consist in the sum of four lines. Four gaussians have been used to fit this spectrum.



FIG. 6. Evolution of the Raman spectrum as a function of *in situ* annealing of the samples. The bottom spectrum is taken from the as-deposited sample. Temperature increases from the bottom spectrum to the top one. (T=410, 470, and 520 K, respectively). Even for moderate thermal treatment a progressive graphitization can be recognized.

 sp^2 disordered carbon films.^{18,21} The low-frequency region is also characterized by features which can be attributed to disordered sp^2 bonds, as reported for different types of carbon.²² The low-frequency region of sputtered *a*-C is characterized by a broad peak at 760 cm⁻¹ which has been related to a peak in the phonon density of states of graphite.²³ Disorder induced Raman scattering was also observed in this region by Li and Lannin in *a*-C and nanocrystalline glassy carbon.²² Laser-deposited amorphous carbon shows similar structures peaked at different energies (500–600 cm⁻¹, 800 cm⁻¹).²⁴ Although the origin of these structures is still a matter of debate, the disorder of a sp^2 carbon network is most likely responsible for the observed spectra.

A moderate annealing of the samples induces changes in the Raman spectra. In Fig. 6, we report the evolution of the Raman spectrum for thermal treatment *in situ* up to 550 K. The resulting trends, as functions of annealing temperature (AT), are as follows. The center of *D* line shows an overall small decrease (from 1362 to 1354 cm⁻¹) and its full width at half-maximum (FWHM) lessens. While the FWHM of the *G* band decreases as well, the peak position is nearly constant around 1585 cm⁻¹. The intensity ratio I_D/I_G grows

from 0.75 to 0.82 while FWHM_G/FWHM_D decreases from 0.6 to 0.5. The 2700 cm⁻¹ peak becomes more definite. We observe a slight growth in I_{1490}/I_T (I_T = total first order intensity) with AT. These trends are consistent with a progressive graphitization and a removal of distorted bond angles and structural disorder.^{24–26} This picture is supported by the trend of FWHM_G/FWHM_D, related to disorder within graphitic bonding and variation in bond angle, which we find to decrease.

The feature around 1180 cm^{-1} deserves particular attention since it has been suggested as related to the sp^3 content in *a*-C films.²⁷ A similar structure has also been reported in films grown with cluster beam deposition in a lower mass range compared to ours, although with a less characterized beam.^{4,12} Perez and co-workers have deconvoluted the Raman spectra in the 1000–2000 cm⁻¹ range with three gaussians only,¹² and they attributed the 1180 cm⁻¹ peak to the presence of a microcrystalline or "amorphous" diamond phase originated by the linking of very small cage-like clusters (C_{28}).¹²

The presence of this amorphous diamond phase in cluster assembled films needs further experimental confirmations. In our samples, the presence of an amorphous diamond phase is unlikely since small cagelike clusters are eventually produced and deposited together with graphitic clusters, thus preventing the formation of a sp^3 network. It has also been shown²⁸ that a model with a small percentage of sp^3 can give density of states (DOS) contributions in this spectral region, without requiring the presence of an amorphous sp^3 phase, which would also probably shift the observed G peak to much lower frequencies. Li and Lannin²² reported a distinct reproducible shoulder in the tail of the D band in glassy carbon which they assigned to a peak at about 1170 cm^{-1} in the corresponding DOS determined by inelastic neutron scattering. Moreover, the observed bump at about 2000 cm^{-1} may be seen as a second order combination of 1180 and 750 cm^{-1} bands, thus indicating that these two modes occur in the same region of the sample which should be graphitelike rather than diamond-like.

Recent quantum molecular dynamics simulations of C_{28} deposition have shown that small fullerenes can act as building blocks of materials characterized by hyperdiamondlike configurations, with only a small portion of sp^3 sites.¹⁰ Vibrational spectra of C_{28} cages suggest that the Raman features around 600 and 1200 cm⁻¹ can originate from the presence of distorted sp^2 bonds (nonhexagonal rings) without invoking diamond phases. Our experiments, although performed with cluster beams in a wide mass range, are in agreement with the calculations, showing that the Raman features are essentially due to disordered sp^2 bonds.

The graphitic nature of the cluster-assembled films is also confirmed by optical spectroscopy. The results of the ellipsometric and reflectance, R, measurements for a 100 nm thick film are shown in Figs. 7(a) and 7(b), respectively. Films with different thicknesses display similar spectral features and lineshapes; the main difference is seen in the position of the reflectance minimum, varying from 2.3 to 2.8 eV. We note that the reflectance calculated by using n and kvalues from ellipsometry agrees with the experimental R



FIG. 7. (a) Refractive index (n) and extinction coefficient (k) of a carbon thin film (solid lines), as measured by ellipsometry; for comparison n and k calculated for a graphite thin film with 0.5 volume fraction of voids (dotted lines) are reported. (b) Reflectance of a carbon thin film on a silicon substrate.

spectrum. This shows two peaks at 3.4 and 4.4 eV, corresponding to the E_1 and E_2 interband transitions of silicon screened by the film, which strongly reduces their intensities. The minimum at about 2.7 eV, where the film is absorbing little, is due to interference between the film and the substrate, and it is strongly dependent on the film thickness.

The *k* spectrum displays a broad peak at 4.3 eV, then it decreases rapidly at lower energies, with an abrupt slope change around 3.2 eV. In correspondence with the peak in *k*, *n* shows a dispersion-like feature, followed by a slight increase with decreasing energy. The *n* and *k* behavior (apart from the absolute values) resembles that of the optical functions of the graphite, for light polarized in the basal planes. In fact, the graphite in this spectral range is characterized by a strong peak in *k* at about 4.7 eV, due to the optical gap at the *Q* point of the Brillouin zone between the bonding π and antibonding π^* electron bands, originated by the p_z orbitals perpendicular to the basal planes.²⁹

It is expected that in a graphite-like film the structural and compositional disorder causes the shrinkage of the π - π^* gap; moreover, a new gap at lower energy can be opened, due to the localization of the π electrons, destroying the semimetallic behavior of graphite.^{30,31} These effects are just evidenced in our optical spectra. In particular, the tail in k below 3 eV has a dependence on the energy E typical of the Tauc model,³² for which $k \propto (E - E_T)^2 / E^2$, yielding an optical gap of $E_T = 0.6$ eV.

We note that our n and k absolute values are much lower than in graphite; this fact can be ascribed to the porous structure of the films, producing a density about half of graphite. We calculated the optical functions of a graphite film with 0.5 volume fraction of voids, in the framework of the

Bruggeman effective-medium approximation,³³ obtaining values of n and k comparable with the experimental ones [Fig. 7(a), dotted lines].

In conclusion, we have deposited and characterized nanocrystalline carbon thin films from supersonic cluster beams. The films are characterized by a low-density, nanoporous structure based on grains with diameters of several tens of nanometers. Raman spectra show that the films are essentially graphitic-like with the presence of a high number of distorted sp^2 bonds. The optical spectra confirm the graphitic structure and show the presence of a gap of 0.6 eV. The granularity of the films may have important consequences on the electronic and mechanical properties of these materials. Localization effects due to the granular structure of the films are currently being investigated. Moreover, the large surface area of these materials can represent an interesting aspect for many technological issues.³⁴ We have also demonstrated that the deposition of cluster beams produced by PACIS sources can be considered as an efficient route towards the production of nanostructured thin films.

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- ¹R. W. Siegel, Mater. Sci. Eng. B **19**, 37 (1993).
- ²H. P. Cheng and U. Landman, Science **260**, 1304 (1993).
- ³H. Gleiter, Prog. Mater. Sci. 33, 223 (1989).
- ⁴P. Melinon, V. Paillard, V. Dupuis, A. Perez, P. Jensen, A. Hoareau, J. P. Perez, J. Tuaillon, M. Broyer, J. L. Vialle, M. Pellarin, B. Baguenard, and J. Lerme, Int. J. Mod. Phys. B **9**, 339 (1995).
- ⁵ P. Milani and P. Piseri, in *Application of Accelerators in Research and Industry*, edited by J. L. Duggan and I. L. Morgan [AIP Conf. Proc. AIP Conf. Proc. **392**, 495 (1997)].

- ⁶I. Yamada, Nucl. Instrum. Methods Phys. Res. 112, 242 (1996).
- ⁷G. A. J. Amaratunga, M. Chowalla, C. J. Kiely, I. Alexandrou, R. Aharonov, and R. M. Devenish, Nature (London) **383**, 321 (1996).
- ⁸H. Sjostrom, S. Stafstrom, M. Roman, and J-F. Sundgren, Phys. Rev. Lett. **75**, 1336 (1995).
- ⁹See, for example, D. R. McKenzie, Rep. Prog. Phys. 59, 1611 (1996).
- ¹⁰A. Canning, G. Galli, and J. Kim, Phys. Rev. Lett. **78**, 4442 (1997).
- ¹¹G. Benedek and L. Colombo, Mater. Sci. Forum 232, 247 (1996).
- ¹² V. Paillard, P. Melinon, V. Dupuis, J. P. Perez, A. Perez, and B. Champagnon, Phys. Rev. Lett. **71**, 4170 (1993).
- ¹³G. Gantefoer, H. R. Siekmann, H. O. Lutz, and K. H. Meiwes-Broer, Chem. Phys. Lett. 165, 293 (1990).
- ¹⁴P. Milani, P. Piseri, and A. Li Bassi (to be published).
- ¹⁵P. Milani and W. A. de Heer, Rev. Sci. Instrum. 61, 1835 (1990).
- ¹⁶P. Piseri, S. Iannotta, and P. Milani, Int. J. Mass Spectrom. Ion Processes 153, 23 (1996).
- ¹⁷C. E. Bottani, A. C. Ferrari, A. Li Bassi, P. Milani, M. Ferretti, and P. Piseri, Carbon (to be published).
- ¹⁸R. J. Nemanich and S. A. Solin, Phys. Rev. B 20, 392 (1979).
- ¹⁹F. Tuinstra and J. L. Koenig, J. Chem. Phys. 53, 1126 (1970).
- ²⁰J. M. Hunter, J. L. Fye, and M. F. Jarrold, J. Chem. Phys. **99**, 1785 (1993).
- ²¹D. S. Knight and W. B. White, J. Mater. Res. 4, 385 (1989).
- ²²F. Li and J. S. Lannin, Appl. Phys. Lett. 61, 2116 (1992).
- ²³W. S. Bacsa, J. S. Lannin, D. L. Pappas, and J. J. Cuomo, Phys. Rev. B 47, 10 931 (1993).
- ²⁴ S. Bhargava, H. D. Bist, A. V. Narlikar, S. B. Samanta, J. Narayan, and H. B. Tripathi, J. Appl. Phys. **79**, 1917 (1996).
- ²⁵ N. H. Cho, D. K. Veirs, J. W. Agers III, M. D. Rubin, C. B. Hopper, and D. B. Bogy, J. Appl. Phys. **71**, 2243 (1992).
- ²⁶J. Robertson, Prog. Solid State Chem. **21**, 199 (1991).
- ²⁷J. Schwan, S. Ulrich, V. Batori, H. Ehrhardt, and S. R. P. Silva, J. Appl. Phys. **80**, 440 (1996).
- ²⁸D. Beeman, J. Silverman, R. Lynds, and M. R. Anderson, Phys. Rev. B 30, 870 (1984).
- ²⁹ A. Borghesi and G. Guizzetti, in *Handbook of Optical Constants of Solids*, edited by E. D. Palik (Academic, New York, 1991), p. 449.
- $^{30}L.$ G. Johnson and G. Dresselhaus, Phys. Rev. B 7, 2275 (1973).
- ³¹M. A. Tamor and C. H. Wu, J. Appl. Phys. 67, 1007 (1990).
- ³² J. Tauc, Amorphous and Liquid Semiconductors, edited by J. Tauc (Plenum, London, 1974).
- ³³D. A. G. Bruggeman, Ann. Phys. (Leipzig) 24, 636 (1935).
- ³⁴See, for example, MRS Bull. XIX (1994).