Radiation-Induced Transformation of Graphite to Diamond

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It is demonstrated theoretically that particle irradiation may lead to a destabilization of graphitic structures with respect to low-pressure growth of diamond. This is due to the large difference in the cross sections for irradiation-induced displacements of carbon atoms in diamond and graphite. A nonequilibrium phase diagram is calculated that shows the stability of graphite and diamond as a function of the displacement rate of atoms. The theoretical results are related to the experimentally observed transformation of spherical graphitic onions to diamond under electron irradiation. [S0031-9007(97)04417-7]

The transformation of graphite to diamond is of considerable technical importance and has been studied both by experiment and theory for several decades. This transformation generally requires high pressures, high temperatures, and, for obtaining reasonable diamond yields, the presence of catalysts. Recent investigations, however, demonstrate that high pressure is not indispensable: As shown experimentally [1] and to be discussed theoretically in the present paper, under the nonequilibrium conditions of intense particle irradiation the graphite-diamond transformation can be carried out at zero pressure and moderate temperatures.

Concentric-shell graphitic onions ("bucky onions") built up of spherical graphene layers may serve as nanoscopic pressure cells for the nucleation of diamond crystals [1]. Such onions form under intense irradiation of graphitic or amorphous carbon with electrons or ions [2]. At irradiation temperatures above 600 K, *in situ* annealing of radiation defects leads to perfectly coherent shells of extreme strength. Because of the loss of atoms resulting from knockon collisions with the irradiating particles [3], the shells contract and exert pressure that increases towards the center of the onions. High pressure and the presence of sp^3 cross-links between the shells eventually lead to the nucleation of diamond crystals in the onion cores (Fig. 1). Once nucleated, these crystals grow under continuing irradiation until almost the whole graphitic onions have transformed to diamond. Since during diamond growth the graphite shells relax and their number decreases, the late stages of the growth process take place at quite low, possibly even at zero pressure [1].

In the present paper, this transformation is generalized and considered from the viewpoint of an irradiation-induced reversal of phase stability in the diamond-graphite system. Comparable modifications of phase stability by irradiation are observed in a large class of solid systems. Examples are order-disorder transitions in metallic alloys or the formation of amorphous and quasicrystalline phases [4]. In the case of carbon, it has been proposed that the higher stability of sp^3 relative to sp^2 sites during irradia-

tion might favor the formation of diamondlike structures during ion deposition [5]. In all these cases, due to the far-from-equilibrium processes that take place during particle irradiation, a phase which is thermodynamically stable under equilibrium conditions transforms into a metastable phase. In general terms, irradiation-induced phase changes may thus be conceived as self-organization phenomena taking place in open nonequilibrium systems [6].

In the case of metallic alloys, a long-standing theoretical effort has been devoted to the calculation of modifications of phase stability and phase evolution due to irradiation (for an overview see [7]). The basic idea of the models is that, in an irradiated phase, atoms may change position not only by thermally activated processes, but also by "ballistic" displacements enforced by the irradiation. This is taken into account using a master-equation description
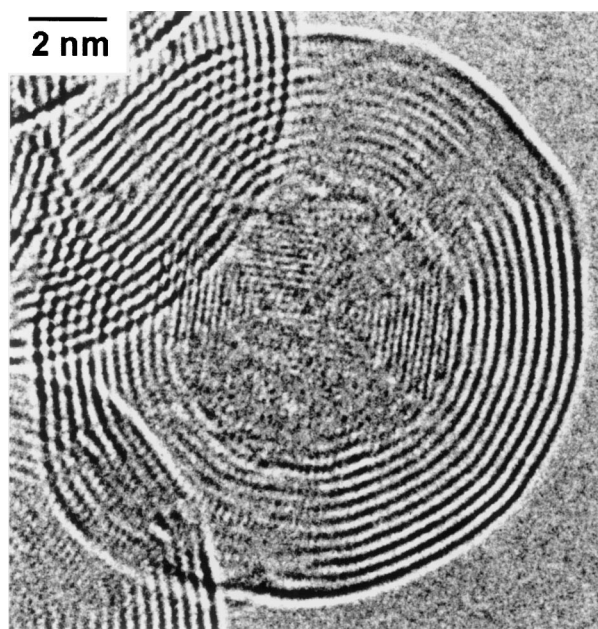

FIG. 1. Transmission electron micrograph of a small spherical concentric-shell carbon onion with a diamond core. The object has developed under electron irradiation at 1000 K.

of the phase-evolution kinetics as worked out in [8]. The models have been developed mainly for coherent phase transitions (e.g., order-disorder transitions) which preserve an underlying lattice structure, i.e., they cannot be applied directly to the graphite-diamond transition. However, we shall demonstrate that a straightforward generalization of the models is possible if nucleation problems are excluded and the phase transformation is considered as the motion of a phase boundary separating two solid modifications of the same element.

We consider a block of N carbon atoms, N_D of which are arranged on the sites of a diamond lattice, while the remaining $(1 - N_D)$ atoms form a graphite lattice. It is assumed that the diamond and graphite phases are separated by a sharp interface. N is taken sufficiently large such that the contribution of the interface to the total Gibbs free energy (we consider conditions of constant pressure) may be neglected. Under irradiation, carbon atoms located at the interface may pass from diamond to graphite, and vice versa, in two manners: (i) They may cross the interface via thermally activated processes. This gives rise to "thermal" jump rates Γ_{th}^{G-D} and Γ_{th}^{D-G} obeying the relationship $\Gamma_{th}^{G-D}/\Gamma_{th}^{D-G} = \exp[-\beta \Delta G]$, where ΔG is the Gibbs free energy difference between diamond and graphite, and $\beta = (k_B T)^{-1}$, in which k_B is the Boltzmann's constant and T is the temperature. Introducing the total rate ν_{th} of thermally activated jumps across the interface gives

$$\Gamma_{th}^{D-G} = p^{D-G} \nu_{th}, \qquad \Gamma_{th}^{G-D} = p^{G-D} \nu_{th}, \qquad (1)$$

where the probabilities p^{D-G} and p^{G-D} are

$$p^{D-G} = \frac{1}{1 + \exp[-\beta \Delta G]},$$
$$p^{G-D} = \frac{\exp[-\beta \Delta G]}{1 + \exp[-\beta \Delta G]}. \qquad (2)$$

In addition to the thermally activated jumps across the interface, under irradiation the ballistic processes may lead to an exchange of atoms between the two phases. Such ballistic jumps take place in two steps: In a first step, carbon atoms are displaced from diamond or graphite lattice sites due to collisions by irradiating particles. In a second step, the thus produced interstitials annihilate on vacant interface or bulk lattice sites of the opposite phase. For describing the resulting jump rates, we make the following simplifying assumptions: (i) Only single interstitials and vacancies are produced by the irradiation (no cascade damage); (ii) exchange of atoms between diamond and graphite is due only to interstitials produced directly at the interface; (iii) the probabilities for an interface interstitial to recombine either on a graphite or a diamond lattice site are governed by the Gibbs free energies of the two phases, i.e., they correspond to the respective probabilities p^{D-G} and p^{G-D} defined in Eq. (2). Then the ballistic jump rates are

$$\Gamma_{irr}^{G-D} = \sigma_G \Phi p^{G-D}, \qquad \Gamma_{irr}^{D-G} = \sigma_D \Phi p^{D-G}, \quad (3)$$

where Φ is the irradiation flux and σ_G and σ_D are the total cross sections for displacement of atoms from the graphite and diamond lattices, respectively. The master equation for the probability P_{N_D} of finding N_D atoms on diamond lattice sites is

$$\frac{1}{N_i} \frac{\partial P_{N_D}}{\partial t} = \Gamma_{tot}^{G-D} P_{N_D-1} + \Gamma_{tot}^{D-G} P_{N_D+1}$$
$$- [\Gamma_{tot}^{D-G} + \Gamma_{tot}^{G-D}] P_{N_D}, \qquad (4)$$

where N_i is the number of atoms at the interface and the total jump rates are $\Gamma_{tot}^{X-Y} = \Gamma_{th}^{X-Y} + \Gamma_{irr}^{X-Y}$ (X-$Y = D$-G or G-D). We consider the solution of this master equation under steady-state conditions. Since we are dealing with a closed system, steady state implies no net flux of matter. For Eq. (4) this requires that the condition of detailed balance, $\Gamma_{tot}^{G-D} P_{N_D-1} = \Gamma_{tot}^{D-G} P_{N_D}$, is fulfilled. It then readily follows that

$$P_{N_D} = \mathcal{N} \exp[-\Psi(N_D)],$$
$$\Psi(N_D) = \Psi(0) + \sum_{0}^{N_D-1} \ln \frac{\Gamma_{tot}^{D-G}}{\Gamma_{tot}^{G-D}}. \qquad (5)$$

Here $\mathcal{N}$ is a normalization constant. In the absence of irradiation, the "stochastic potential" Ψ corresponds to the Gibbs free energy of the system divided by $k_B T$. By analogy, for the irradiated system a nonequilibrium "effective free energy" G_{eff} can be defined which governs phase stability under irradiation. The difference in the effective free energies per atom on the diamond and graphite lattice is $\Delta G_{eff} = k_B T [\Psi(N) - \Psi(0)]/N$. Using Eqs. (1) to (5) one finds

$$\Delta G_{eff} = \Delta G - k_B T \ln \left[\frac{1 + \Phi \sigma_G/\nu_{th}}{1 + \Phi \sigma_D/\nu_{th}} \right]. \qquad (6)$$

In the absence of irradiation ($\Phi = 0$) as well as at high temperatures ($\nu_{th} \gg \sigma_D \Phi, \sigma_G \Phi$) where a thermal exchange of atoms across the interface prevails, ΔG_{eff} reduces to the Gibbs free energy difference ΔG. On the other hand, during irradiation at not too high temperatures ballistic jumps are predominant ($\nu_{th} \ll \sigma_D \Phi, \sigma_G \Phi$). Provided that the cross section for ballistic displacements of atoms from the sites of the diamond lattice is smaller than that for displacements from graphite lattice sites, $\sigma_G/\sigma_D > 1$, this leads to a reduction of the nonequilibrium effective free energy of the atoms in the diamond lattice by an amount of about $k_B T \ln[\sigma_G/\sigma_D]$ with respect to the Gibbs free energy.

The impact of irradiation on a crystalline structure can be characterized by the displacement threshold energy E_d, i.e., the minimum energy that must be transferred to a lattice atom to induce its permanent displacement. While in diamond, E_d is of the order of 35 eV [9] and only weakly anisotropic, in graphite the threshold energy is strongly direction dependent. Our own irradiation experiments on graphitic carbon nanostructures revealed values of $E_d = 10-20$ eV, depending on the type of irradiated

structure. While $E_d = 10$ eV can be considered an appropriate value for displacements along the c axis, a larger value of $E_d \approx 20$ eV applies to the case of isotropic irradiation. Calculations of the displacement cross sections in diamond and graphite performed with these E_d values indicate that at electron energies less than about 150 keV permanent displacements can be induced in graphite but not in diamond, $\sigma_G/\sigma_D = \infty$. This ratio decreases with increasing electron energy, but is still $\sigma_G/\sigma_D \approx 2$ at electron energies of about 1.5 MeV. Thus the necessary condition for an irradiation-induced inversion of phase stability, $\sigma_G/\sigma_D > 1$, is well fulfilled.

Further parameters entering the effective free energy difference ΔG_{eff} are the difference ΔG in the Gibbs free energies, the rate ν_{th} of thermal jumps of atoms across the interface, and temperature. We assume $\nu_{\text{th}} = \nu_0 \exp \times [-\beta G_i]$ to be governed by an Arrhenius law, where ν_0 is an attempt frequency and G_i is the characteristic free activation energy required for crossing the interface. In our calculations, we took the characteristic value $\nu_0 = 10^{12}$ s^{-1} and an activation enthalpy of the order of typical bond energies, $G_i = 4$ eV [10]. For calculating the Gibbs free energy differences, we used the experimental values of $\Delta G(T)$ at zero pressure and the atomic volumes compiled in [10].

With these parameters, calculations of the effective free energy difference ΔG_{eff} were performed for different displacement cross-section ratios. Under irradiation, diamond is more stable than graphite provided that $\Delta G_{\text{eff}} < 0$. Using this criterion, nonequilibrium phase diagrams at zero pressure have been calculated. In Fig. 2, phase boundaries are given in terms of temperature and irradiation intensity, where the latter is characterized by the rate $\sigma_G \Phi$ of atomic displacements in graphite. [The unit "dpa" (displacements per atom) is the irradiation dose required to displace, on the average, each atom once from its lattice site.] It is seen that reversal of phase stability takes

place in an intermediate temperature range, the extension of which depends on the irradiation intensity as well as on the ratio of the total displacement cross sections. The mechanism leading to phase stability reversal may be rationalized as follows: At the interface, ballistic displacements lead to the production of interstitials which stem predominantly from graphite lattice sites. If for these interstitials the probabilities to relax into diamond or graphite lattice configurations are of the same order of magnitude, this already causes a net flux of atoms from the graphite to the diamond phase, i.e., the phase stability is reversed.

If T exceeds an upper critical temperature, thermal jumps, which lead to a net transport of matter from diamond to graphite, predominate over the ballistic ones, so that graphite remains the stable phase. In Eq. (6) this is manifested by the fact that for large ν_{th} the nonequilibrium correction is too small to make ΔG_{eff} negative. At lower temperatures, the thermal jump rate soon becomes quite small. Provided that T exceeds a lower critical temperature, the nonequilibrium term, which is then approximately $k_B T \ln[\sigma_G/\sigma_D]$, may cause a change in the sign of ΔG_{eff}, i.e., a phase-stability reversal. The lower critical temperature is almost independent on the irradiation intensity, but strongly dependent on the ratio of the displacement cross sections (Fig. 2). If the energy of the irradiation is such that atoms are displaced in graphite but not in diamond, the phase stability may be changed even at very low temperatures.

An important question concerns the rate of transformation. From the master equation (5) an expression for the average transformation rate of graphite to diamond, or vice versa, may be deduced. This can be expressed in terms of the velocity v of the motion of the diamond-graphite interface. In a coordinate system fixed to the graphite lattice, this is given by $v = (\Gamma_{\text{tot}}^{G\text{-}D} - \Gamma_{\text{tot}}^{D\text{-}G})b$, where $b = \Omega^{1/3}$ (Ω is the atomic volume of graphite). A positive v corresponds to the growth of the diamond phase. In Fig. 3,
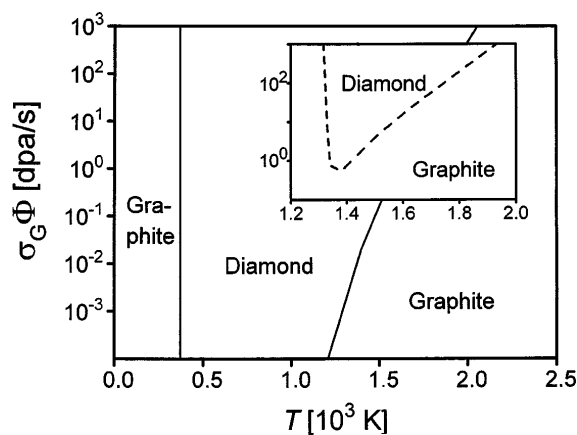

FIG. 2. Nonequilibrium phase diagram (irradiation intensity vs temperature) of the diamond-graphite system under electron irradiation; displacement cross section ratio $\sigma_G/\sigma_D = 3$ (full line), $\sigma_G/\sigma_D = 2$ (inset, dashed line); for other parameters see text.
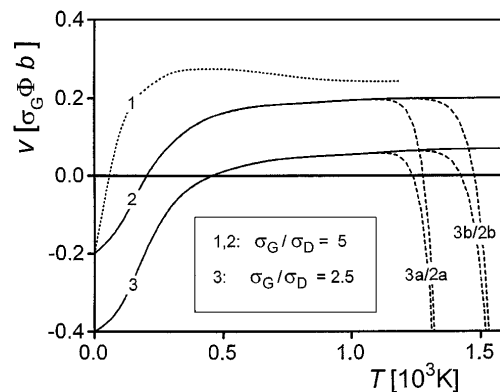

FIG. 3. Velocity v of the diamond-graphite transformation as a function of temperature for two different displacement cross-section ratios; irradiation intensity $\sigma_G \Phi = 10^{-2}$ dpa/s (curves 2a/3a), 1 dpa/s (curves 2b/3b); dotted line (curve 1): Modification of v for $\sigma_G/\sigma_D = 5$ by a hydrostatic pressure of 1 GPa; negative v indicates graphite growth.

the temperature dependence of v is depicted for two different values of σ_G/σ_D and different irradiation intensities. The zeros of v correspond to the critical parameters for phase-stability reversal. It is interesting to note that irradiation, which at intermediate temperatures leads to diamond growth, at low temperatures actually promotes the transformation of diamond to graphite. (In the absence of irradiation, this would be "frozen in" because of the negligibly small thermal jump rates.) Except in the vicinity of the upper critical temperature (dashed lines in Fig. 3), the transformation velocity is proportional to the displacement rate, irrespective of the direction of the transformation. At a typical displacement rate of $\sigma_G\Phi = 10^{-1}$ dpa/s during irradiation in a high-voltage electron microscope and for $b = 2.1$ Å, one finds that a value of $v \approx 0.2\sigma_G\Phi b$ characteristic of $\sigma_G/\sigma_D = 5$ and $T \approx 1000$ K corresponds to a diamond growth rate of about 15 nm/h.

The theoretical results in Figs. 2 and 3 match well the experimental data that have been measured up to date. Under electron irradiation in an electron microscope, in graphitic onions displacement rates up to 0.1 dpa/s were attained. A ratio of displacement cross sections of $\sigma_G/\sigma_D = 5$ has been estimated [1]. The transformation has so far been investigated at 300 K and in the range 675–1000 K. The growth velocity of the diamond core was $v \approx 30$ nm/h at 1000 K and a displacement rate of the order of magnitude of 0.1 dpa/s. It decreased by a factor of 10 to 20 when the beam intensity was reduced by a factor of 10. Diamond growth within the graphitic onions was found to take place in an almost isotropic manner with the diamond-graphite interface nearly parallel to the graphitic basal planes, but without preferential orientation with respect to the diamond lattice.

At 300 K neither growth nor shrinkage ($v = 0$) of the diamond cores was observed. Increasing the temperature from 675 to 1000 K results in an increase of the growth velocity of the diamond core by a factor of 2. Under constant temperature and radiation flux, a slight decrease in growth velocity is observed during diamond growth. Since hydrostatic pressure is expected to accelerate the graphite-diamond transition (dotted line in Fig. 3), this is attributed to the decreasing pressure exerted by the outer shells of the graphitic onions.

The present theory predicts that the graphite-diamond transformation under irradiation, provided that a diamond nucleus is present, should not only take place in graphitic onions, where the anisotropy is constrained, but also in planar graphite. This still has to be confirmed experimentally. However, the transformation from hexagonal to cubic *boron nitride* (isostructural to graphite and dia-

mond, respectively) under electron irradiation was already achieved, even without the presence of onionlike structures [11]. As to graphitic onions with diamond core, the theory reproduces all essential qualitative features of their behavior during irradiation. These are the existence of a temperature regime where diamond growth may be observed and the dependence of the growth velocity on irradiation intensity and temperature. The calculated values of the lower critical temperature and the diamond growth velocity are in qualitative agreement with the experimental data. Further experiments will be able to review the theoretical model and refine the underlying parameters. From a theoretical point of view, further work is required to account for the influence of point defects produced in the bulk of the graphite and diamond phases and recombining at the interface. In particular, the pronounced anisotropy of interstitial diffusion in graphite, where the basal planes act as diffusion barriers, may be crucial for understanding the observed orientation of the interface during diamond growth.

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