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Ordering of gas bubbles during light ion gas implantation

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Abstract. There have been interesting observations about ordering of microstructures during irradiation. The formation of void lattices is amongst the better known examples. Ordering has also been observed in small gas filled bubbles formed during low energy light ion implantation in the energy range 30–100 keV.

The basic underlying mechanism for ordering of gas bubbles has not been clearly understood so far. We identify in this paper a basic instability in the growth kinetics of such bubbles which can develop during irradiation. This instability is shown to be associated with the interstitial production due to the high pressure inside these bubbles and their differential bias due to the strain field interactions with vacancies and interstitials. It is shown that such an instability leads to a selection of a wavelength scale which agrees with the observed lattice parameter.

Keywords. Bubble lattice; ion implantation; micro-structure; ordering; bifurcation.

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1. Introduction

The extended defects like voids, gas filled bubbles and dislocation loops are known to develop into ordered periodic structures during irradiation (Jaeger *et al* 1987; Evans 1971; Johnson and Mazey 1980a, b). In general, the periodic array develops from an initially random distribution of microstructure which evolves during irradiation. In the initial stage no spatial correlations exist, but emerge on continuation of irradiation. Finally, a periodic pattern results with a well defined characteristic wavelength or lattice constant of a superlattice. Further, these periodic defect arrays are found to be parallel to the host lattice structure which indicates the existence of a strong influence of the host lattice crystallography.

Void lattices have been observed in many metals like molybdenum, tungsten, niobium, tantalum, nickel and aluminium (Evans 1971; Stoneham 1971; Krishan 1982a, b) formed by about 5 MeV ion irradiation or fast neutron irradiations done at temperatures higher than one third of the absolute melting point. Typically, the voids are a few tens of angstroms in diameter and are separated by 200–700 Å. Superlattices of gas filled bubbles form by room temperature implantation of about 30–100 keV ions of insoluble gases like helium or hydrogen. The bubbles are usually about 20–30 Å in size and the superlattice spacing is in the range of about 70 Å which implies their concentration to be as high as 10^{19} cm^{-3}. Recently, Jaeger *et al* (1987) have made an interesting observation on the formation of periodic defect walls along the soft [100] type directions of the fcc matrix of copper and nickel when exposed to a 3 MeV

proton beam at room temperature. On further analysis they found these walls to consist of point defect clusters like stacking fault tetrahedra and (vacancy) dislocation loops of about 300 Å diameter and the superlattice spacing observed was about 600 Å.

Although several attempts have been made to explain the ordering of the extended defects, the basic understanding is far from complete. Malen and Bullough (1971) have attempted to solve the problem of void lattice formation by assuming the major interaction between voids to arise from the elastic strain field around them. Following Willis and Bullough (1969), they have used the information that the cubic anisotropy of the host lattice elasticity leads to the stability of the void lattice. Starting from the same basic model Stoneham (1971) has computed the total energy of the void lattice. The host lattice structure is naturally taken into account in his analysis and the superlattice parallel to the host lattice turns out to be stable. They have pointed out that correcting the possible deficiencies in their calculation would improve the numerical results on the stability of the void lattices. More recently Dubinko *et al* (1989), Dubinko (1991) have given models for void and bubble lattice formation based on elastically induced directional absorption of point defects by self-interstitial dislocation loops. Since the loops can glide only along specific crystallographic directions the model quite naturally leads to an ordered lattice with the correct crystallographic symmetry.

However, another important aspect of the phenomenon which is not dealt with in these studies is the evolution of the periodic array from the initial random distribution. Krishan (1980, 1982a, b) has explained the emergence of this spatial order on the basis of non-equilibrium phase transition where the kinetics of the point defects coupled with their interaction with the microstructure, and in particular the vacancy loops produced from cascades, is responsible for such a phenomenon. In the case of bubble lattices, the 30–100 keV light ion irradiations do not produce any cascades and hence vacancy loops which played a crucial role in the theoretical model for void ordering are, however, absent. The objective of this paper is to show that the over-pressurized bubbles in fact result in an equivalent coupling as in the case of vacancy loops. This gives rise to an instability which leads to a bifurcation from a random to a periodic structure. The parametres responsible for this instability will be identified and it will be shown that the typical wavelength of the periodic structure is consistent with the observed lattice parameter. A simple form of the model is presented to explicitly bring out the main behaviour of the instability. However, since we will be dealing with the homogeneous rate equations, the question of crystallographic symmetry will not be dealt with in this paper.

2. Rate equations for bubble growth

During the implantation the concentration c_g of the implanted gas atoms keeps increasing; concurrently the concentration c_v of vacancies and c_i of the interstitials also change continuously. The interaction of these irradiation produced point defects leads to the formation of bubbles due to agglomeration. Once the microstructure develops, it acts as a sink for the point defects and influences the evolution of the defect concentrations. Using the homogeneous rate theory the time evolution of c_v

can be written as

$$\frac{dc_v}{dt} = K - D_v \rho c_v + D_v \nabla^2 c_v \tag{1}$$

where K represents the rate of vacancy production due to displacement damage by the implanted ions, D_v the vacancy diffusion coefficient and ρ the bubble sink strength which is written (Brailsford and Bullough 1972; Rauh *et al* 1981) as $4\pi Nr$ in terms of the average bubble radius r and the number density N of the bubbles. In (1) the second term refers to the rate at which vacancies are lost to the bubbles and are gained by diffusion according to the last term. Similar consideration for the interstitial concentration c_i leads to

$$\frac{dc_i}{dt} = K(1+\varepsilon) - ZD_i \rho c_i + D_i \nabla^2 c_i. \tag{2}$$

Here the two important parameters introduced are ε, the fraction of interstitials produced due to emission from the over-pressurized bubbles and Z, the preference of the bubbles for absorptions of interstitials over vacancies. The sink bias Z and the emission rate ε both depend on the internal gas pressures P in the bubbles and form an important aspect of the present theoretical model. We will give a detailed evaluation of these parameters in § 4. The interstitial diffusion coefficient is given by D_i. On the other hand, the gas pressure P arises from the gas concentration build up at a rate

$$\frac{dc_g}{dt} = K_g - D_g \rho c_g + D_g \nabla^2 c_g \tag{3}$$

where the different quantities with subscript 'g' refer to the gas atoms. This equation gives the kinetics of gas concentration in the matrix. A portion $D_g \rho c_g$ enters the bubbles contributing to the gas pressure build up in the cavities which in turn influences the value of Z and ε as will be modelled in § 4. The quantity $D_g \rho c_g$ contributes to the gas pressure build up in the bubbles which in turn influences the values of Z and ε as a second order effect. The above equation is coupled to the earlier equations only through these variables. For the purpose of the present problem involving the late stages of bubble growth, when Z and ε almost saturate, we treat them as constant parameters evaluated in the steady state.

We now turn to the equation for the bubble growth. The bubbles grow by absorbing vacancies and shrink by absorbing interstitials as may be seen in the rate equation

$$\frac{dq}{dt} = D_v \rho c_v - ZD_i \rho c_i + \varepsilon K \tag{4}$$

written for the total bubble volume fraction $q = 4\pi Nr^3/3$.

3. Stability analysis

We now carry out a stability analysis of the rate equations (1), (2) and (4). Let c_{v0}, c_{i0}, q_0 (and ρ_0) be the steady state (fixed point) values of these quantities obtained by setting the respective rates equal to zero. We now seek a solution in the

neighbourhood of the fixed point (c_{v0}, c_{i0}, q_0). Let δc_v, δc_i and δq be small deviations from the fixed point. Substituting these variables in the rate equations and taking the Fourier transform

$$\delta c_v(r) = \int \delta C_v(k) \exp(ik \cdot r) \mathrm{d}^3 k \tag{5}$$

etc., we rewrite the rate equations in terms of the Fourier components represented by the respective capital symbols. With this, the rate equations become

$$\frac{\mathrm{d}\delta C_v}{\mathrm{d}t} = -D_v(\rho_0 + k^2)\delta C_v - D_v C_{v0}\delta\rho, \tag{6a}$$

$$\frac{\mathrm{d}\delta C_i}{\mathrm{d}t} = -D_i(Z\rho_0 + k^2)\delta C_i - D_i C_{i0}\delta\rho, \tag{6b}$$

$$\frac{\mathrm{d}\delta Q}{\mathrm{d}t} = D_v \delta C_v \rho_0 - ZD_i\rho_0\delta C_i + (D_v C_{v0} - ZD_i C_{i0}). \tag{6c}$$

Here δC_v and δC_i correspond to the fast diffusing species and therefore can be adiabatically eliminated from the above equations. This approach is consistent with the fact that the rates associated with these variables rapidly approach zero. Setting the rates in (6a) and (6b) equal to zero we obtain δC_v and δC_i in terms of $\delta\rho$. Substituting these results in (6c) and rearranging terms we get

$$\frac{1}{\delta\rho}\left(\frac{\mathrm{d}\delta Q}{\mathrm{d}t}\right) \equiv R(k) = \frac{k^2[(Z-1-\varepsilon)\rho_0 - \varepsilon k^2]}{\rho_0(\rho_0 + k^2)(Z\rho_0 + k^2)}. \tag{7}$$

From the definition of q and ρ (as given in § 2) we observe that $\delta q = \rho^2\delta\rho/16\pi^2N^2$. In the Fourier representation $\delta Q = \rho_0^2\delta\rho/16\pi^2N^2$ where the steady state sink strength ρ_0 has been used. Substituting this in (7) and on integrating we obtain

$$Q(k,t) = \delta Q(k,0)\exp\left(\frac{16\pi^2N^2}{\rho}R(k)\cdot t\right).$$

Thus the dynamics of $\delta Q(k,t)$ is determined by the sign of $R(k)$ and therefore $R(k)$ is identified as the amplification factor for the mode k. Further, it can be seen that under those irradiation conditions where $(Z-1) < \varepsilon$, $(1/\delta\rho)(\mathrm{d}\delta Q/\mathrm{d}t)$ has a negative value over the range of all real values of k (which is physically meaningful). This implies that all these Fourier components of the bubble distribution diminish in magnitude with time. So all the modes of the bubble distribution are unstable and the distribution continues to be in the homogeneous state. However, when $(Z-1) > \varepsilon$, there is a range of k between O and k_1 where $(1/\delta\rho)(\mathrm{d}\delta Q/\mathrm{d}t)$ is not only positive but also passes through a maximum at $k = k_m$ when plotted against k^2. This is schematically shown in figure 1. This means that all the Fourier components with wave vector k less than k_1 will grow with time. The values of k_1 and k_m are given, respectively, by $R(k) = 0$ leading to

$$k_1^2 = \left(\frac{Z-1-\varepsilon}{\varepsilon}\right)\rho \tag{8}$$

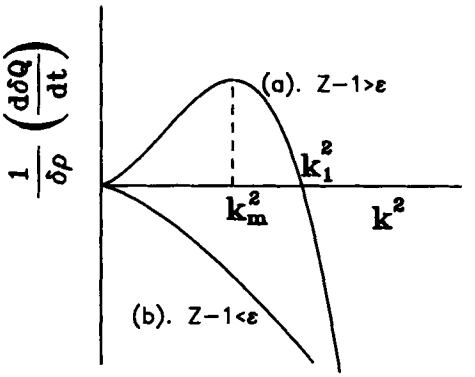

Figure 1. The mode amplification rate $(1/\delta\rho)(d\delta Q/dt)$ as a function of the wave vector k for the condition (a) $(Z-1)>\varepsilon$ and (b) $(Z-1)<\varepsilon$.

and

$$\frac{\partial R(k)}{\partial(k^2)}=0 \text{ leading to}$$

$$k_m^2=\frac{\sigma Z-\sigma-\varepsilon}{\varepsilon Z+Z-\varepsilon} \tag{9}$$

where $\sigma=[(\varepsilon+1)/Z]^{1/2}$. The negative value of $R(k)$ implies that the amplitude of the other components of the initial distribution with $k>k_1$ will diminish as the irradiation continues. It may be noted that the mode with $k=k_m$ will grow fastest and therefore, this mode will emerge as the dominant mode to eventually manifest as the superlattice structure with a periodicity (or lattice constant) A_0 given by

$$A_0=\frac{2\pi}{k_m}. \tag{10}$$

Such a superlattice will appear amidst a more or less diffuse background of bubble distribution arising from the modes having k values different from k_m. The eventual superlattice structure is characterized by the lattice constant A_0 which is a function of the kinetic parameters ε and Z. As has already been discussed, ε and Z control the coupled kinetics represented by (1), (2) and (4) and affects a bifurcation depending on whether $(Z-1)$ is less than or greater than ε.

4. The model for ε and Z

As discussed in the previous section, the vacancies and the interstitials produced during irradiation by atomic displacement are responsible for the development of the bubbles. When the bubbles become over-pressurized with the implanted gas atoms the elastic strain energy favours emission of interstitials at a rate $K\varepsilon$ as represented in (2). Similarly, the different manner in which the vacancies and the interstitials interact with the bubbles is reflected in the bias factors Z_v and Z_i. The relative bias factor Z of the interstitials over the vacancies used in the (2) above is given by Z_i/Z_v.

The parameters ε and Z are unfortunately not amenable to direct experimental measurement; they have therefore to be modelled. In this section we present a model for estimating these parameters from basic considerations of the physical processes associated with the formation and growth of the bubbles.

4.1 *Evaluation of* ε

A typical bubble is essentially a cluster of n_v vacancies containing n_g number of gas atoms at a pressure P. So, a triad (n_v, n_g, P) may therefore be employed to denote such a bubble. The volume of such a bubble, assumed to be spherical is given by

$$V(n_v) = n_v\Omega = \frac{4\pi}{3} r_1^3 \tag{11}$$

where Ω is the atomic volume and r_1 is the radius of the bubble. The surface energy of this bubble is

$$\Gamma_1 = S(n_v)\cdot\gamma = 4\pi r_1^2\gamma \tag{12}$$

here S is the surface area of the bubble and γ is the surface energy of the material. We assume that on acquisition of $\tilde{n}$ number of additional gas atoms the bubble is over-pressurized to $P + \delta P$. This may be represented by the reaction

$$(n_v, n_g, P) + \tilde{n} \rightarrow (n_v, n_g + \tilde{n}, P + \delta P). \tag{13a}$$

Let such an over-pressure be just sufficient to emit an interstitial. Thus, the over-pressurized bubble further transforms to a bigger bubble by emitting an interstitial (i) through the reaction

$$(n_v, n_g + \tilde{n}, P + \delta P) \rightarrow (n_v + 1, n_g + \tilde{n}, P) + i. \tag{13b}$$

The volume and surface energy of the bubble after growth are

$$V(n_v + 1) = V(n_v) + \Omega = \frac{4\pi}{3} r_2^3 \tag{14}$$

and

$$\Gamma_2 = \Gamma_1 + \delta\Gamma = 4\pi r_2^2\gamma \tag{15}$$

respectively, where r_2 is the radius of this bubble. Now balancing the energies in (13b) one can derive

$$V(n_v)\delta P = \Omega P + \delta\Gamma + E_i \tag{16}$$

where E_i represents the interstitial formation energy. On the other hand, using the simple equation of state ($PV = RT$) for the bubbles in different stages represented in (13a) and (13b) one can write

$$V(n_v)\delta P = \tilde{n} k_B T. \tag{17}$$

Comparison of (16) and (17) yields

$$\tilde{n} = \frac{\Omega P + \delta\Gamma + E_i}{k_B T}. \tag{18}$$

In order to make an estimate of the rate at which interstitials are emitted from the bubbles it is useful to connect the rate dn_g/dt at which a bubble acquires gas, the displacement damage rate K and α the number of interstitials produced per helium ion incident. This is done by

$$\frac{dn_g}{dt} = \frac{K}{\alpha}. \tag{19}$$

This gives the rate at which gas accumulates inside a bubble. This should be distinguished from (3) which gives the rate of gas accumulation in the matrix. In fact, the term $D_g.\rho.c_g$ appearing in (3) should be equal to $N(dn_g/dt)$. However, K can be easily estimated from the radiation damage inflicted during ion implantation. Therefore it is convenient to use (19) independent of (3). If all the bubbles are assumed to be of the same size the rate of interstitial emission from the bubbles is given by

$$K\varepsilon = \frac{dn_g}{dt}\frac{1}{\bar{n}}. \tag{20}$$

Using (18) and (19) in (20) one can write,

$$\varepsilon = \frac{k_B T}{\alpha(\Omega P + \delta\Gamma + E_i)}. \tag{21a}$$

Now we shall make a numerical estimate of ε for a typical experimental situation (Johnson and Mazey 1980a). For the case of 30 keV helium implantation into nickel at 300 K, $\alpha = 20$ and $k_B T = 0{\cdot}025$ eV. For a typical bubble (of radius $r = 10$ Å) where the gas pressure is about 7 GPa†, the value of $\Omega \times P$ can be estimated to be about 0·47 eV. The value of the surface energy for nickel is about 20 kg/m and this gives $\delta\Gamma = 0{\cdot}71$ eV. Similarly, we take the interstitial formation energy $E_i = 1{\cdot}5$ eV. Using these value in (21a), ε can be estimated to be

$$\varepsilon = 4 \times 10^{-4}. \tag{21b}$$

4.2. *The bias factor Z*

The different elastic strain fields around the vacancies and the interstitials lead to different strength of interaction with the extended defects. This has attracted the attention of many investigators. Here we follow Wolfer and Askin (1975) for estimating the individual defect bias factors Z_v and Z_i. Ignoring the negligibly small strain field produced around the bubbles, the point defect bias factor Z_d for the over-pressurized

† Such a value of pressure can be estimated from the high density equation of state (EOS). Evans (1977) has given an empirical isotherm ($T = 300$ K) based on the EOS proposed by Rowlinson (1963),

$$P = 0{\cdot}492\exp(5{\cdot}15 \times 10^{-23}.n_{He})$$

where n_{He} is the number of helium atoms per cc and P is in kbar. For a gas density of about 1–2 atoms per vacancy P is estimated to be about 7 GPa.

bubbles can be written as

$$Z_d = 1 - \frac{3\mu_d \Delta P^2}{56 k_B T G^2} \tag{22}$$

where the subscript d denotes either v or i for vacancies or interstitials as the case may be, μ_d is the elastic polarizability of the defect d, G is the shear modulus ($\simeq 10^{10}\,\mathrm{kg/m^2}$) and $\Delta P = P - (2\gamma/r)$. Equation (22) implies that the point defect bias factors vary with the pressure inside the bubbles but it can be shown that the pressure sensitivity of Z_i is considerably higher than that of Z_v. For a value of gas pressure of 7 GPa inside a bubble (of radius $r = 10$ Å) in nickel (where the surface tension $\gamma \simeq 20\,\mathrm{kg/m}$), the over-pressure $\Delta P \simeq 3\,\mathrm{GPa}$. The elastic polarizabilities of the primary point defects are in the range of $\mu_v \simeq -15\,\mathrm{eV}$ and $\mu_i \simeq -150\,\mathrm{eV}$. With these values of the material and defect properties, an estimate of Z_d can be made as

$$Z_v \simeq 1{\cdot}029 \tag{23a}$$

and

$$Z_i \simeq 1{\cdot}290 \tag{23b}$$

which results in a value of the relative bias factor

$$Z = \frac{Z_i}{Z_v} = 1{\cdot}25. \tag{24}$$

This means that the self-interstitials interact with the bubbles about 25% more strongly than the vacancies do. This estimate is a rough first order estimate. For a more correct estimate higher order terms in (22) should also be retained. Under the influence of an external stress field the value of Z will further get somewhat altered. This is known to give rise to the stress affected swelling in materials irradiated under stress. However, in the present case we consider a stress-free condition where Z has been estimated to be 1·25.

4.3 *The superlattice*

The model parameters ε and Z used in the rate equations (1) and (2) influence the coupled kinetics of c_v, c_i and q. This leads to the eventual emergence of an ordered pattern of spatial bubble arrangement. The influence of ε and Z on the superlattice parameter A_0 is seen in (9) and (10) above. The model values of ε and Z as given by (21b) and (24) are seen to satisfy the condition $(Z-1) > \varepsilon$. Thus the kinetics will lead to a peaking of $R(k)$ in (7) at $k = k_m$ as suggested by (9). This involves the sink strength ρ which is estimated to be $\rho = 4\pi N r \cong 1{\cdot}22 \times 10^{14}\,\mathrm{cm^{-2}}$. Now the k_m can be directly evaluated from (9) and the superlattice constant A_0 from (10). This is estimated to be about 100 Å which is in the same order of magnitude as the experimentally observed value of about 70 Å.

5. Summary and discussion

A simple model has been developed to treat the coupled kinetics of the primary defects produced during low energy light gas ion irradiation. The microstructure of gas

bubbles are shown to be differentially biased towards interstitials as compared to the vacancies. Also the bubbles being over-pressurized, they emit interstitials over and above the interstitials produced by displacement damage. Such a system is shown to exhibit a microstructural instability and it bifurcates to an ordered structure. The instability is controlled by the parameters Z and ε; and for $(Z-1) > \varepsilon$ the homogeneous state becomes unstable and spatial correlations develop resulting in the emergence of a characteristic wavelength corresponding to the spatially ordered structure.

The basic point defect equations explicitly include diffusion mechanism (and therefore involve the diffusion coefficients D_v and D_i). However, the subsequent results such as the amplification factor $R(k)$ or the superlattice wave vector k_m do not depend on D_v or D_i showing an insensitivity to the irradiation temperature which is consistent with the experimental observation. Of course, in the actual case there will be other neutral sinks such as grain boundaries or cavities with very low gas pressures (and hence exhibit negligible biasing). In such a case, eqs (1) and (2) get modified to

$$\frac{dc_v}{dt} = K - D_v(\rho + \rho_n)c_v + D_v\nabla^2 c_v \tag{25}$$

and

$$\frac{dc_i}{dt} = K(1+\varepsilon) - D_i(Z\rho + \rho_n)c_i + D_i\nabla^2 c_i \tag{26}$$

where ρ_n is the neutral sink strength. However, eq. (4) for the bubble growth rate remains unchanged. This influences the final result of k_m and the control parameter $(Z-1)/\varepsilon$ depends on ρ. However, for demonstrating the main features of this method, the simple model presented in this paper is sufficient.

Further, it may be noted that the results obtained are isotropic. The superlattice constant A_0 is only an average value and does not indicate the crystallographic relationship of the superlattice with the host lattice. This, however, is to be expected as no structural information about the host lattice has been incorporated into the rate equations. The underlying anisotropy of the host lattice can possibly be incorporated through the tensor forms of the diffusion constants, the interstitial emission fraction ε and the bias factor Z. As these parameters are not amenable to direct measurement, they have to be modelled by taking the crystallographic anisotropy into account.

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