Strain Anisotropy in Freestanding Germanium Nanoparticles Synthesized by Ball Milling

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Although embedded Ge nanocrystals (NCs) have been grown by variety of techniques and its properties have been studied extensively, intrinsic properties of isolated Ge NCs have not been studied properly due to lack of proper synthesis technique. Here we report on the synthesis of freestanding Ge nanoparticles (NPs) down to $\sim 7$ nm using ball milling technique and study its structural evolution as a function of milling time. Morphology and microstructure of the freestanding Ge NPs are studied using atomic force microscopy, transmission electron microscopy and X-ray diffraction (XRD) analysis. A systematic study of the XRD line profile using Williamson–Hall method reveals presence of anisotropic strain in the milled NPs. Strain anisotropy factor is calculated using a modified Williamson–Hall method by taking into consideration a dislocation contrast factor, assuming that dislocations are main contributors to the strain in these NPs. Our calculations suggest that screw type dislocations are main contributors to the strain anisotropy in the Ge NPs. We find that for milling time up to 40 hrs, NPs size monotonically goes down to $\sim 7.3$ nm and then almost saturates, while the dislocation density first increases from $1.64 \times 10^{16} \text{ m}^{-2}$ to $11.62 \times 10^{17} \text{ m}^{-2}$ for milling time up to 20 hrs and then decreases drastically during further milling. We have monitored a low temperature heat release at $\sim 310 \text{ } ^{\circ}$C from the milled NPs using differential scanning calorimetry, clearly indicating a kind of structural relaxation of the strained NPs.

Keywords: Ge Nanoparticle, Strain Anisotropy, Ball Milling, Microstructure, XRD Line Profile.

1. INTRODUCTION

Ge nanocrystals (NCs) have attracted considerable attention because of its potential applications in non-volatile memory and integrated optoelectronics, as well as the prospect for discovering new physical phenomena. In contrast to Si NCs, Ge NCs are expected to show stronger confinement effect due to its large excitonic Bohr radius ($\sim 17$ nm). A number of groups have reported synthesis of Ge NCs in amorphous SiO2 matrices.1 However, embedding matrix is known to strongly influence the structural and optical properties of the embedded Ge NCs.2 In order to understand and exploit the intrinsic properties of Ge NCs, it is important to study Ge NCs that are freestanding or isolated. There have been very few attempts to study the structural and optical properties of freestanding Ge NCs, primarily due to lack of suitable technique to synthesize freestanding Ge NCs.

Ball milling is a powerful technique for large scale production of freestanding nanoparticles (NPs) and other nanostructures.3 However, very little is known about the microstructure of such freestanding Ge NPs. Broadening in XRD line profile is usually used to calculate crystallite size and strain in nanocrystals.4 Ungar et al.5–9 suggested a powerful method of XRD line profile analysis that takes into account anisotropy in strain and it enables precise determination of particle size, strain and mechanism of strain in nanocrystals. This method has been applied successfully to study varieties of nanomaterials.10,11 However, to our knowledge, no studies have been reported on the strain analysis on Ge NPs.

In this work, we report on the synthesis of Ge NPs down to size $\sim 7$ nm using ball milling technique and study its microstructural evolution as a function of milling time. A detailed analysis using XRD line profile is presented to calculate the strain anisotropy factor in the Ge NCs. The results of the analysis are supported by atomic force microscopy (AFM), transmission electron microscopy (TEM) and differential scanning calorimetric (DSC) measurements. We also discuss the structural relaxation of the strained NPs during low temperature heating.

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2. EXPERIMENTAL DETAILS

To prepare the Ge NPs, high purity (99.999%) Ge powder (Sigma Aldrich) with initial particle sizes below 150 μm are mechanically milled in a planetary ball mill (Retsch, PM 100) for duration up to 40 hours in a zirconium oxide vial filled with small balls of zirconium oxide. This ensures that no metallic contaminants are introduced during milling process. The milling was performed under normal atmospheric condition. The powder to ball ratio was taken as 1:20 and the ball mill was operated at 350 rpm. Ultra fine Ge NPs obtained after various stages of milling are studied for the evolution in the microstructural properties. The powder sample was analyzed by high resolution XRD measurements (Bruker, Advance D8). The data were collected in slow scan mode for the careful determination of average crystallite size, internal strain and dislocation density in the milled powder using Williamson–Hall method and the method suggested by Ungar et al. An AFM (Agilent, Pico SPM II Molecular Imaging) was used to study the size and morphology of the milled NPs. A 200 KV ultra high resolution TEM (JEOL-2010) was used to study the nanocrystallite size and microstructure of the ball-milled NPs. DSC measurements were carried out with a commercial calorimeter (Perkin Elmer, DSC-7).

3. RESULTS AND DISCUSSION

3.1. AFM Studies

Gradual reduction in particle size as a result of ball milling was monitored after every 5 hrs of milling. Figures 1(a–c) show typical AFM and TEM images of the Ge NPs obtained after milling time of 5 hrs and 20 hrs. Using AFM analysis, average size of NPs calculated from Figure 1(a) is ~21.9 nm for 5 hr milling and that of Figure 1(b) is ~12 nm for 20 hrs milling. TEM image of Figure 1(c) shows that the most of the NPs have size in the range 10–12 nm, though a few are of larger size. The size reduces further with increasing milling time. Both from AFM and TEM studies on different regions of the deposited NPs (on a suitable holder), we find a large distribution in size of the Ge NPs. Both the AFM and TEM images show that the shapes of the NPs are non-spherical, such as oval or dumbbell shape. It is due to the high speed grinding that the initial spherical particles breaks into non-spherical shapes and strain is developed in the milled NPs due to deformation.

3.2. XRD Pattern Analysis

Figure 2 depicts the XRD patterns obtained from Ge powders after each step of milling for 5 hrs. Full width at half maxima (FWHM) of the XRD pattern was calculated by fitting Lorentzian line shape to the experimental data. The gradual broadening of the width of the reflections shown in Figure 2 can be attributed to the reduction in average crystallite size and strain induced in the milling process.

3.2.1. Structural Analysis Based on Williamson–Hall Method

According to the Williamson–Hall (WH) method, the individual contribution to the broadening of reflection shown in Figure 1 can be expressed as

\[ \beta \cos \theta = \frac{2.35 \lambda}{D_{WH}} + 4\varepsilon \sin \theta \]  

(1)

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Fig. 2. XRD pattern for milled Ge NPs showing gradual broadening of Bragg peaks with increasing milling time, due to size reduction and development of strain. Instrumental broadening is subtracted from measured line width for line profile analysis.

where $\beta$ is the FWHM of the Bragg peaks (in radians), $\theta$ is the Bragg angle of the analyzed peak and $\lambda$ is the wavelength of the X-ray ($\lambda = 0.154056$ nm for Cu-K$_\alpha$). $D_{WH}$ is the average crystallite size and $\epsilon$ is the strain. All Ge reflections within a $2\theta$ range of 20° to 60° were used to construct a linear plot of $\beta \cos \theta$ versus $4 \sin \theta$, as shown in Figure 3. The experimental data were corrected for instrumental broadening. It is evident from the scattered data in Figures 3(a–c) that the data do not entirely obey the WH formulation for three different samples obtained after 5, 10, and 20 hrs of milling. Data for nanocrystalline material often fail to obey the Williamson–Hall plot. The deviations are larger when the material being studied is elastically anisotropic because the residual strains affect some Bragg reflections more than the others. The deviation observed in our data is due to existence of anisotropic variation in the residual strain. If we ignore the strain anisotropy effect to calculate crystallite size and strain using Eq. (1), we obtain very large values of particle size and strain from the data as shown in Figure 4. Due to a large scatter in the data in Figure 3, calculation of intercept is erroneous and thus unrealistic values of particle sizes are obtained, as compared to the sizes obtained from AFM and TEM studies.

3.3. Structural Analysis Based on Ungar et al. Method

Ungar et al. suggested that the introduction of a dislocation contrast factor in Eq. (1) might result in better fit to the data. According to Ungar et al., Eq. (1) can be expressed as

$$\Delta K = \frac{0.9}{D_U} + \Delta K^D$$

(2)

$$\Delta K^D = 2eKC^{1/2}$$

(3)

where $\Delta K = (2 \cos \theta_b \Delta \theta_b)/\lambda$, $\Delta \theta_b$ is FWHM (in radians) of the Bragg reflections, $\lambda$ is wavelength of X-rays, $D_U$ is the average crystallite size, $K = 2 \sin \theta_b/\lambda$, $e$ is strain, $C$ is the dislocation contrast factor and $\Delta K^D$ is the strain contribution to line broadening, respectively. In the conventional WH plot it is assumed that $\Delta K^D$ has the form of a linear or a quadratic function of $K$. It has been shown that in the case, when strain is caused by dislocations, $\Delta K^D$ has the

Fig. 3. Williamson–Hall plot for (a) 5 hrs, (b) 10 hrs, (c) 20 hrs milled NPs. The experimental data do not follow a linear fit (dashed line), as evident from scattered data points (symbols) in the plot.

Fig. 4. Average crystallite size ($D_{WH}$) and lattice strain ($\epsilon$) as a function of milling time. The dashed lines are guide to the eye. The $D_{WH}$ and $\epsilon$ values are extracted from Figure 3, assuming a linear fit. Due to inappropriate fit, the calculated size is very large compared to average size obtained from AFM and TEM analysis.
following form:9
\[
\Delta K^0 = A (\rho^*)^{1/2} + A' (Q^*)^{1/2} \tag{4}
\]
where \( \rho^* \) is the formal dislocation density, \( Q^* \) is related to two-particle correlations in the dislocation ensemble, \( A \) and \( A' \) are parameters determined by the effective outer cutoff radius of dislocations. If the dislocations are main contributions to the strain then Eq. (2) can be expressed as9
\[
\Delta K = 0.9/D_0 + (\pi b^0 \rho/2B)^{1/3} (K_C^{1/2})
\]
\[
+ (\pi b^0 Q/2B)^{1/2} (K_C^{1/2}) \tag{5}
\]
where \( b \) is modulus of the Burgers vector of dislocation, \( \rho \) is the average dislocation density, \( C \) is the average contrast factors, \( B \) and \( B' \) are constants. The constant \( B \) is taken as 10 for a wide range of dislocation distribution.\(^9\)

Equation (5) shows that the proper scaling factor of the FWHM (\( \Delta K \)) of the line profile is \( K_C^{1/2} \) instead of merely \( K \). The \( C \) factor incorporates the anisotropy factor in strain. This is usually referred as modified Williamson–Hall method.

Equation (5) shows that if the contribution of 2nd order term is much less compared to 1st order term in (\( K_C^{1/2} \)), the plot of \( \Delta K \) versus \( K_C^{1/2} \) would follow nearly a straight line.

It has been shown that for a cubic crystal, the average contrast factors (\( C \)) are linear functions of the fourth order invariant of the \( hkl \) indices of the different reflections:\(^9\)
\[
C = C_{\text{iso}}(1 - \eta H^2) \tag{6}
\]
where \( H^2 = (h^2 k^2 + h^2 l^2 + k^2 l^2)/(l^2 + k^2 + l^2) \) \tag{7}
and \( C_{\text{iso}} = A_4[1 - \exp(-A_2/B)] + A_3 + \delta \tag{8}
A_4 = 2 C_{\text{iso}}(C_{11} - C_{12}) \tag{9}
\]
For cubic material, the contrast factor \( C_{000} \) depends on the Burger and line vectors characterizing the dislocations, the elastic anisotropy \( A_4 \) and the ratio \( C_{12}/C_{44} \), where \( C_{11}, C_{12} \), and \( C_{44} \) are the elastic constants. For Ge, \( C_{12}/C_{44} = 0.649 \) and \( A_4 = 1.651 \). We use a computer program to calculate the values of \( C_{000} \) for different types of edge and screw dislocations using the known elastic constants for Ge. For edge dislocation we find that: \( \alpha = 0.1425, \beta = 1.642, \gamma = 0.0198, \delta = 0.0947 \), and for screw dislocation: \( \alpha = 0.174, \beta = 1.952, \gamma = 0.0295, \delta = 0.0662 \). With these values, \( C_{000} = 0.21388 \) for screw dislocation, and \( C_{000} = 0.217753 \) for edge dislocations. Thus, average value comes out as \( C_{000} = 0.21582 \). In Eq. (6) combined with Eq. (5), the unknown parameters are \( q, D_0, A_4, \) and \( \rho \). The unknown parameter \( q \) is obtained by plotting \( K_C^{1/2} \) versus \( \Delta K \) and adjusting the \( q \) value such that the data points follow a linear fit. In this way, we obtain: \( q \approx 1.79 \) for different reflections. In some cases we obtained slightly higher values for a better linear fit. A lower value of \( q \) yields a highly nonlinear plot. The \( q \) value of \( \sim 1.8 \) or higher indicates that the nature of the dislocations involved is basically screw type in the milled Ge NPs.\(^8\)

Figure 5 shows the plot of \( K_C^{1/2} \) versus \( \Delta K \) for three different milling times and it demonstrates the quality of the fit obtained for the present data using the above method. For comparison, both the linear and quadratic fits are shown for the experimental data. Since the quadratic function more describes the functional dependence more accurately, we extracted the parameters (\( D_0, \rho \)) from the quadratic plot. The average dislocation density \( \rho \) and the average crystallite size \( D_0 \) calculated from the quadratic plot are shown in Figure 6. The linear fit data which neglects the 2nd order term of \( K_C^{1/2} \) slightly overestimates the particle size for low milling time samples. Figure 6 shows that the average crystallite size slowly goes down from 22.0 nm (5 hrs) to \( \sim 7.4 \) nm (30 hrs) and then slightly increases (to 8.5 nm) for further milling in wet condition. On the other hand, dislocation density first goes up to \( \sim 11.62 \times 10^{16} \) m\(^{-2} \) for milling time of 20 hrs and then drastically reduces to 0.08 x 10\(^{16} \) m\(^{-2} \) for 30 hrs milling. We notice that during wet milling (beyond 30 hrs milling) the particle size slightly grows, while the dislocation density again goes up drastically for longer duration milling. An increase of strain with the size reduction (as a result of milling) is quite expected. However, the reduction of strain or dislocation density after 20 hrs of milling is most likely to be caused by in-situ heating during prolonged

\( \Delta K = 0.9/D_0 + (\pi b^0 \rho/2B)^{1/3} (K_C^{1/2}) + (\pi b^0 Q/2B)^{1/2} (K_C^{1/2}) \tag{5} \)
milling. The particle sizes obtained from the above analysis are in excellent agreement with the sizes found from AFM and TEM analysis. Our results demonstrate that the modified Williamson–Hall method i.e., the Ungar et al. method is very appropriate for XRD line profile analysis of mechanically processed nanocrystalline powders, where one can isolate the contribution of nanocrystallite size and strain very accurately. In our milled Ge NPs, the dislocations are primarily of screw type as determined by the q value. As a result of milling, screw type dislocations are expected to occur in a planetary ball mill where both the balls and grinding jar rotate at a high speed. This action rapidly accelerates the grinding balls through both centrifugal and Coriolis force. The rapid acceleration of the particles from one side of the jar to the other produces powerful impact forces between the balls and sample material while also providing additional grinding action through frictional forces. Due to rotational motion, a twist is produced in the crystal and thus screw type of dislocations is formed.

The strain (proportional to dislocation density) calculation shows that NPs produced after 20 hrs of milling has maximum strain. Note that in Figure 5(c), the quadratic fit to data for Ge_20 sample has a negative curvature as compared to the fit for 5 hrs and 10 hrs milled samples. This may imply that due to large strain in this sample, a kind of structural transformation is occurring after 20 hrs of milling. For milling beyond 20 hrs, there is a structural relaxation in Ge NCs and the calculated dislocation density reduces as shown in Figure 6.

3.4. DSC Studies

In order to verify the presence of strain, we performed DSC measurement on the 20 hrs milled sample and the result is shown in Figure 7. The inset of Figure 7 shows the differentiated heat flow curve allowing proper determination of temperature for the heat release. The data clearly show low temperature heat releases at ~313 °C and ~398 °C upon heating from room temperature up to 550 °C. Though the crystallization temperature of amorphous Ge is above the range of heating temperature, in nanocrystal of Ge one may expect a lower temperature of crystallization. It has been reported that due to availability of large numbers of surface atoms the melting point of semiconductor nanoparticles (freestanding) is relatively low as compared to their bulk crystal counterpart.12 In the present case, we relate the low temperature heat release to structural relaxation in Ge NCs. In the strained NCs, the distortion in bond angle and bond length is likely to recover during heating and the exothermic process is a signature of relaxation of local structure of Ge NCs. Similar low temperature structural relaxation has been reported from pure amorphous Ge produced by ion-irradiation.13 A measurable amount of the low temperature heat release also suggests that strain is very high in the 20 hrs milled Ge NPs, in agreement with the XRD line profile analysis. There has been report of complete amorphization of Ge NPs after milling.14 Our results do not suggest amorphization for milling up to 40 hrs. However, it indicates presence of large strain in the NPs. There is likelihood of growing pockets of amorphous regions in the Ge NCs for long duration milling. More studies are under progress to understand the microstructure in such cases.

4. CONCLUSIONS

We have synthesized freestanding Ge NPs of size ~7 nm by ball milling technique and studied the structural evolution in the NPs as a function of milling time. XRD line profile analysis reveals presence of anisotropic strain in the Ge NPs. A detailed analysis incorporating dislocation contrast factor for the strain is found to describe the experimental data successfully. Our analysis shows that
ball milling produces primarily screw type of dislocations in the Ge NPs. The strain is found to gradually build up with the reduction of size up to 20 hrs of milling, and beyond 20 hrs of milling the strain drastically goes down. Again above 30 hrs of milling under wet condition the strain goes up, though the particle sizes monotonically goes down and achieves saturation after 30 hrs of milling. The presence of large strain is verified by DSC analysis, which shows a low temperature (∼310 °C) heat release upon heating from room temperature. The particle size calculated from XRD analysis is in excellent agreement with AFM and TEM analysis.

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References and Notes


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