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The role of size effects on the crystallization of amorphous Ge in contact with Bi nanocrystals

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The kinetics of metal-induced crystallization of amorphous Ge in contact with Bi nanocrystals (NCs) have been studied by *in situ* transmission electron microscope annealing. Series of nanostructured films consisting of layers of Bi NCs in an amorphous Ge matrix have been grown by pulsed laser deposition. The *a*-Ge crystallization temperature depends strongly on both the size and shape of the NCs and the separation between the NCs in the film-normal direction. The size of the NCs controls the crystal nucleation process through the amount of metal surface in contact with the semiconductor, the shape of the NCs determines the initial Ge crystallization in the direction perpendicular to the film plane, and the separation between the NCs in the film-normal direction controls the overall pattern of the Ge crystal growth process. © 1998 American Institute of Physics. [S0021-8979(98)04021-3]

I. INTRODUCTION

Nanostructured materials containing metal nanocrystals (NCs) exhibit a number of interesting and novel properties related to the small size of the NCs (typically around 10 nm or below) which are different from those of conventional polycrystalline materials or amorphous solids.¹ Although the technological interest in nanostructured materials relies mainly on their special mechanical, magnetic, or optical properties, they also exhibit characteristic thermophysical properties. The depression of the melting point of small metal particles with respect to that of the bulk metal has been widely reported,² as has the fact that the diffusivity of typically immiscible elements (such as Bi in Cu) is substantially enhanced in nanocrystalline materials.³

Size effects have been observed upon annealing nanostructured materials containing metal NCs in a glassy matrix. Most of the works report a change of the diameter of the NCs upon annealing,^{4–7} and a decrease of the melting temperature when the radius of the NCs is increased.^{5,8,9} Some of these effects are very sensitive to the environment in which the annealing is performed.^{4,5} Changes to the structure of the NCs⁹ and analysis of the stability and crystallization of the matrix,⁷ however, have been much less frequently reported. Size effects have also been observed in layered systems; for instance, the temperature of crystallization of amorphous Ge (*a*-Ge) films sandwiched between SiO_x layers was found to increase as the film thickness was decreased in the range 1–5 nm,¹⁰ whereas the temperature of crystallization of *a*-Ge films in contact with a Pb layer was found to increase with increasing *a*-Ge thickness, or with decreasing thickness of the contact Pb layer.¹¹ These effects have important implications regarding the stability of the nanostructured systems and should be carefully analyzed together with the mechan-

ical, magnetic, and optical behavior of these systems in order to optimise the performances of potential devices.

Amorphous semiconductors are known to crystallize at temperatures well below their normal crystallization temperature when in contact with metals, with crystallization temperatures of the order of 0.7–0.8 of the eutectic temperature of the metal/semiconductor system.^{12,13} This effect, which is usually known as metal-induced crystallization (MIC), has been extensively studied in layered systems, but very rarely in systems in which metal NCs are embedded in a semiconductor matrix. It has been acknowledged that interdiffusion at the interface between the metal and the semiconductor plays an important role in the crystal nucleation,^{14,15} with the degree of interdiffusion being enhanced by the presence of a high density of grain boundaries and/or defects. Indeed, in the layered materials it has been found that the crystallization temperature of *a*-Ge in contact with Bi is lower for small grain systems than for large grain size ones,¹⁶ and this is thought to be due to a difference in the interface energy. However, the crystal growth in both cases occurs by the same “interface-controlled” mechanism. This means that although the *growth* process cannot be related to grain boundary interdiffusion, the *nucleation* process can, and a similar mechanism might apply in the case of NCs embedded in a matrix.

The aim of the present investigation is thus to study the role of size effects on the crystallization of a *layered* system consisting of discrete Bi NCs and spacer layers of *a*-Ge. The effect of the NC size and shape, and of the spacer layer thickness on the thermal stability of *a*-Ge has been studied. We have used *in situ* transmission electron microscopy (TEM) annealing for the present study and quantitative analysis of the results of the annealing experiments has been carried out using the phenomenological Avrami equation.^{17–19} The crystal front velocity and the activation energy for growth, E_g , have also been determined.

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TABLE I. Deposition parameters used for growing the Bi/Ge layered films.

Sample series	B _x G ₁₀₀ I	B _x G ₁₀₀ II	B ₂₄ G _y III	TB _x G ₁₀₀ IV
Number of pulses on target for element with constant layer thickness	Ge y = 100	Ge y = 100	Bi x = 24	Ge y = 100
Number of pulses on target for element whose thickness is varied	Bi (x)	Bi (x)	Ge (y)	Bi (x)
	12	0	200	12
	25	18	400	24
	50	24	600	36
	100	30	800	48
	200	36	...	60
	...	42	...	72
	...	48	...	...
	...	54	...	...

II. EXPERIMENTAL METHODS

The Bi/Ge samples were grown by pulsed laser deposition (PLD) and are nanocomposite films of Bi clusters embedded in an *a*-Ge matrix. This technique was used because it has recently shown a great deal of success in depositing thin layered films containing metal nanoparticles.^{20,21} Alternate laser ablation of pure Bi and Ge targets was performed in vacuum ($<10^{-5}$ Pa) by focusing an ArF laser (12 ns, 193 nm, 2 J/cm²) onto the targets. The size of the Bi NCs and the thickness of the spacer layers of *a*-Ge were varied by changing the number of laser pulses on the Bi and Ge targets, respectively. Most of the films were grown in a multilayer configuration in which Bi was deposited first, followed by *a*-Ge, with the Bi/Ge sequence being repeated five times. The films will be referred to as B_xG_yZ, where *x* and *y* indicate the number of laser pulses on the Bi and Ge layers within the series Z. Table I summarizes the different film configurations. Note that for comparison purposes an *a*-Ge film with no nanocrystals was made under the same conditions as series II and therefore is included in Table I as B₀G₁₀₀II. The films were deposited simultaneously onto carbon-coated mica (mica/C) and Si substrates kept at room temperature. The C layer acted as a "release" layer which allows the films to be floated off the mica easily in distilled water to prepare plan-view TEM specimens. The samples deposited on Si substrates were used to measure the Bi and Ge concentrations by Rutherford backscattering spectrometry (RBS), using a 2.0 MeV ⁴He⁺ beam. The detector was set at a scattering angle of 185°. Finally, in order to study the crystallization kinetics for films in which possible interactions between different Bi layers do not exist, a series of trilayer films (TB_xG₁₀₀IV) with the configuration mica/C/Ge/Bi/Ge was deposited.

The microstructure of the as-grown films was studied using high resolution electron microscopy (HREM) in a JEOL 4000EX with a point-to-point resolution of 0.16 nm. Annealing of the films was performed by controlled heating *in situ* in a JEOL 4000EX TEM (0.25 nm point-to-point resolution). The annealing temperatures were measured by a thermocouple mounted in the heater body and the results were recorded onto video tape using a Gatan television/image pickup system. Some *in situ* annealing experiments

FIG. 1. Plan-view HREM image of the as-grown B₅₄G₁₀₀I film. The dark contrast regions in which crystal lattice fringes can be observed correspond to the Bi NCs.

were also performed in diffraction mode and in this case the diffraction patterns were recorded onto film. Quantitative analysis of single frames extracted from the video tapes was carried out using the Semper image processing package and from this analysis the crystal front velocity, activation energy, and growth of the transformed areas with time, could be determined. Further details of the *in situ* annealing experiments and the quantitative analysis techniques used can be found elsewhere.²² Post-annealing studies of the microstructure were carried out using a JEOL 200CX TEM.

III. RESULTS

A. As-grown films

Figure 1 shows a plan-view image of the B₅₄G₁₀₀I film. The image shows dark crystalline features (the Bi NCs) superimposed on a random background (the *a*-Ge). The Bi NCs are oval in shape, and as the number of pulses on Bi increases the NCs become bigger. In order to estimate the size of the NCs the average diameter of the NCs, defined as the mean of the large and short axes, has been measured from the HREM images. Figure 2(a) shows the average diameter of the NCs measured for several of the series I and series II films. The size of the NCs increases with the number of pulses, and the size of the NCs in films of series II is consistently slightly smaller than in series I. It should be noted that the different series were not grown one immediately after the other and the laser conditions (laser beam

FIG. 2. (a) Mean diameter of the Bi NCs, and (b) areal density of Bi (●), (▲) and Ge (○), (△) atoms as a function of the number of laser pulses used on the Bi target per layer, for the $B_xG_{100}I$ films with $x \leq 50$ (○), (●) and the $B_xG_{100}II$ films (△), (▲). The dashed lines correspond to linear fits of the data.

shape and degree of focusing) can change slightly after weeks of operation, resulting in slightly different deposition rates for each series. Preliminary annealing results obtained from films of series I (i.e., $B_xG_{100}I$) showed that the films from which the greatest information about the crystallization kinetics of the semiconductor matrix can be obtained are those deposited using 50 pulses or lower on the Bi target, which results in a NC size lower than 10 nm. For this reason the $B_xG_{100}II$ series was grown with $x \leq 54$.

Figure 2(b) shows the areal density of Bi and Ge atoms in the series I and series II B_xG_{100} films, obtained from the RBS measurements. The areal density of Bi atoms in both series follows a linear dependence on the number of pulses and is higher for series I than for series II. The areal density of Bi atoms in series II agrees with the HRTEM observation that the NCs are smaller for series II [see Fig. 2(a)]. The difference in the total number of deposited Bi atoms in the two series is not very large when a small number of pulses is used, but becomes more important as the number of pulses is increased. The areal density of Ge atoms for each series remains approximately constant, as expected from the constant number of pulses in the Ge target for each series, and is higher for series I than for series II since a change in laser conditions will affect both components in the same way. The data shown in Fig. 2(b) can be used to determine the at. % of Bi (i.e., the Bi/Ge ratio) in each film. This value is essentially the same for a given number of Bi and Ge pulses in both series. In spite of the differences in the growth conditions, the results in Figs. 2(a) and 2(b) show that films from series I and II have very similar features, specially those grown with a small number of laser pulses on the Bi target.

FIG. 3. (a) Areal density of Bi (▲) and Ge (△) atoms, and (b) average thickness of the *a*-Ge layer between the Bi NCs as a function of the number of laser pulses used on the Bi target per layer, for the $B_{24}G_xIII$ films. The dashed lines correspond to linear fits of the data.

Figure 3(a) shows the areal density of Bi and Ge atoms in the films for series $B_{24}G_yIII$, obtained from the RBS measurements. Film $B_{24}G_{100}III$ corresponds to film $B_{24}G_{100}II$, i.e., it is the same film. Note that for this series the varying parameter is the number of pulses on the Ge target per layer, and therefore the number of total Bi atoms now remains constant for all the films in the series. It is clearly seen that the total number of Ge atoms increases linearly with the number of pulses on the Ge target. Figure 3(b) shows the average thickness of the Ge layers in between the Bi NCs, calculated from the areal density of Ge atoms [Fig. 3(a)], assuming the density of bulk Ge (4.4×10^{22} atoms/cm³) and that the five layers have the same thickness. As expected, the average thickness of the layers increases linearly with the number of pulses on the Ge target. Making the same assumption the thickness of the Ge spacing layers for the films of series I and II can also be calculated. The Ge average layer thickness is ~ 3.0 nm for series I and ~ 1.5 nm for series II. Note that all the samples of series II have the same Ge thickness per layer as film $B_{24}G_{100}III$ [see Fig. 3(b)].

Prior to *in situ* TEM annealing the microstructure of the films was checked using TEM. Films with more than 50 pulses for Bi from series I, and more than 36 pulses for Bi from series II showed crystallization of the *a*-Ge at room temperature within several months after deposition—the higher the number of pulses for Bi the sooner the film crystallized. This spontaneous crystallization shows that the stability of the films with large Bi NCs is poor. The remaining films with low Bi content have shown no crystallization at room temperature since their deposition (15 months for series I films and 6 months for series II).

FIG. 4. Diffraction patterns from the $B_{25}G_{100}I$ film (a) as-grown and (b) after crystallization of the a -Ge.

B. *In-situ* annealing experiments

In situ constant-heating-rate annealing experiments were performed in the TEM in diffraction mode on the films that showed no spontaneous a -Ge crystallization at room temperature when these experiments started ($B_xG_{100}Z$ samples with $x \leq 54$). The temperature was increased at a rate of ~ 20 K min^{-1} , and the temperature at which the first halo in the diffraction pattern, arising from the amorphous material, sharpened was recorded. Sharpening of the ring indicates crystallization of the a -Ge. Typical diffraction patterns before and after crystallization of the Ge layers in $B_{25}G_{100}I$ are shown in Fig. 4. In Fig. 4(a) only diffuse halos corresponding to the a -Ge are visible, because the Bi NCs are too small (2.5 nm in diameter) to contribute to the diffraction pattern. In Fig. 4(b) a series of rings is visible, which can be indexed as corresponding to crystalline Ge with the diamond cubic structure. The rings that are observed are indicative of the formation of polycrystalline Ge with a relatively small grain size.

A plot of the crystallization temperature of the Ge versus number of laser pulses for the Bi is shown in Fig. 5. As can be seen there is a very large change in the crystallization temperature of the Ge with the number of pulses on Bi, and thus with Bi particle size. Data obtained for series $B_xG_{100}I$ and $B_xG_{100}II$ are both included. The corresponding crystallization temperature for a Ge film with no Bi nanocrystals ($B_0G_{100}II$) is also included for comparison. The results clearly show that the films with the lowest Bi content are the most thermally stable, but their crystallization temperature always remains below that of the Ge film with no nanocrystals. It is also seen that the relationship between crystallization temperature and number of pulses on Bi per layer is not linear—a change in the number of pulses on Bi per layer has a greater effect on the a -Ge crystallization temperature when the number of pulses on Bi is low. A comparison of the a -Ge crystallization temperatures for the series I and series II films gives a measure of the size of the Bi NCs in the series II films relative to those in the series I films. As can be seen, the crystallization temperature for a given series II film is about 20 K higher than the crystallization temperature for the series I film deposited with the same number of pulses on Bi. This difference in crystallization temperature agrees with the

FIG. 5. Crystallization temperature of a -Ge as a function of the number of laser pulses used on the Bi target per layer, and thus as a function of the Bi particle size, for the $B_xG_{100}I$ films with $x \leq 50$ ($\circ$) and the $B_xG_{100}II$ films ($\triangle$). The crystallization temperature for the reference a -Ge film with no Bi nanocrystals $B_0G_{100}II$ is also included on the vertical axis ($\blacktriangledown$). The dashed line is a guide to the eye.

slightly smaller size of the NCs in series II compared to series I, as discussed in Sec. III A and shown in Fig. 2(a). Thus crystallization temperature can be used to give a measure of Bi NC size in the films.

Isothermal annealing experiments were performed on the series I and II films with $x \leq 30$, over the temperature ranges shown in Table II. Although the temperatures at which crystallization occurred were different for each film (as shown in Fig. 5) qualitative and quantitative analysis of the experimental data showed that the crystallization process is the same for all the films. Figure 6 shows single video frame images of the $B_{25}G_{100}I$ film recorded during *in situ* TEM crystallization [Figs. 6(a)–6(c)] together with a TEM image of the film after crystallization [Fig. 6(d)]. The video images show the growth of circular crystalline regions which reach a size of ~ 5 μm in diameter. The TEM image recorded after crystallization [Fig. 6(d)] shows that the Ge in the circular crystalline regions is polycrystalline with a grain size of 5–35 nm. Crystal growth proceeds with a constant crystal growth velocity, implying an interface-controlled growth mechanism, with the growth being radial rather than straight.

TABLE II. Range of crystallization temperatures used for the isothermal annealing experiments for the various films.

Film	Temperature range (°C)
$B_{12}G_{100}I$	380–400
$B_{25}G_{100}I$	284–340
$B_{12}G_{100}II$	400–500
$B_{18}G_{100}II$	353–422
$B_{24}G_{100}II$	320–379
$B_{30}G_{100}II$	284–332

FIG. 6. Images of the $B_{30}G_{100}II$ film taken from single video frames recorded during *in situ* TEM annealing at 312 °C after (a) 11 s, (b) 18 s, and (c) 25 s, showing an increase in size of circular crystalline Ge regions; (d) a higher magnification dark-field TEM image of the film after crystallization.

The Avrami exponent, n ,^{23,24} was determined for each film by quantitative analysis of the data recorded on the videotape. As the annealing temperature was increased there was an increase in the Avrami exponent, n , from $2.5(\pm 0.2)$ at the

FIG. 7. Crystallization temperature of a -Ge as a function of the number of laser pulses used on the Ge target per layer, and thus as a function of the average thickness of the a -Ge layer between Bi NCs for the $B_{24}G_xIII$ films. The dashed line is a guide to the eye.

lowest annealing temperature in each case to $5.5(\pm 0.2)$ for the highest annealing temperature. The activation energy for growth, E_g , was determined from an Arrhenius plot of the crystal growth velocity with temperature and an average value for the different films studied is $1.2(\pm 0.6)$ eV.

In order to study the effect of changing the thickness of the Ge spacer layers between the layers of Bi nanocrystals, *in situ* constant-heating-rate (~ 20 K min^{-1}) anneals were also carried out on the $B_{24}G_yIII$ films in diffraction mode. The results of these experiments are shown in Fig. 7. As can be seen, as the thickness of the a -Ge increased the temperature required to crystallize the film increased dramatically to start with. However, above 400 pulses on the Ge target per layer the a -Ge crystallization temperature tends to a saturation value. Isothermal anneals carried out on the series III multilayer films showed that the crystallization process proceeded in a way similar to that described above for the series I and II films, i.e., radial growth of circular crystalline Ge areas, except for series III films with the thicker Ge layers ($B_{24}G_{600}III$ and above). For these films, following the appearance of crystal nuclei, only very limited crystal growth in the plane of the layers was observed. Crystallization of the film occurred via the formation of many crystal nuclei at random positions across the film, which eventually covered the whole area of the film.

In order to assess whether the crystallization phenomena in these nanocomposite films depend on the presence of a three-dimensional array of NCs the crystallization temperature of series $TB_xG_{100}IV$ was investigated. Constant-heating-rate annealing experiments carried out on the series IV films showed that the crystallization temperature of the Ge decreased with increasing Bi content, similar to what was observed for the series I and II multilayer films. However the crystallization temperatures were always higher than those for the multilayer films with the same nominal size of Bi NCs. Furthermore, the crystallization temperature of the $TB_{24}G_{100}IV$ film, 560 °C, is higher than that of any of the

series III films. No quantitative analysis of isothermal anneals performed on the trilayer films could be carried out because the low total film thickness resulted in poor contrast being observed in the TEM images, but the crystallization was observed to occur via the formation of many nuclei and limited crystal growth, in the same way as seen for the series III films with the thicker Ge layers.

IV. DISCUSSION

The fact that there is a large change in *a*-Ge crystallization temperature with metal NC size, and that the Ge is crystallizing at temperatures well below that of a thin *a*-Ge film with no NCs embedded (see Fig. 5) indicate that MIC of the Ge is occurring. Indeed for films with large Bi NCs, MIC together with lattice strain introduced by the presence of the large NCs, has led to crystallization of *a*-Ge at room temperature after a period of a few months, a phenomenon that is never observed in *a*-Ge films with no NCs, even after several years. This result suggests that as the size of NCs is increased, so the activation energy for nucleation of crystallization for the Ge, E_n , is decreased. These results are consistent with previous work carried out on Ge/Bi layered systems which have shown that there is enhanced resistance to MIC for films in which the Bi layers are composed of large grains [referred to as large grain systems (LGS)] compared to those in which the Bi grains are small [small grain systems (SGS)].¹⁶ This was ascribed to an increase in roughness of the Ge/Bi interfaces for the SGS films, resulting in a larger surface area of Bi in contact with the Ge and in a higher defect density at the interfaces.²⁵ If the small grains in the SGS films are now separated one obtains a particulate layered system such as that analyzed in the present study, in which the Bi surface area in contact with the Ge is increased even further. As is observed, these films do indeed show a lower resistance to MIC than the layered films analyzed earlier. However, as the number of NCs and their size is decreased, i.e., the total amount of Bi in contact with the semiconductor is decreased, the resistance to MIC should increase again in agreement with our experimental observations. This progression is summarized in Fig. 8 which shows the variation in *a*-Ge crystallization temperature with the characteristic Bi crystal size. We have included in this plot the data corresponding to the films with NCs from this work (taken from Fig. 5), and the crystallization temperatures reported in Ref. 16 for the SGS and LGS Ge/Bi layered systems. This figure clearly shows that size effects are extremely important in the MIC of *a*-Ge and that the decrease in the crystallization temperature is proportional to the amount of surface area of the metal in contact with the semiconductor. It should be noted that although this figure shows very well the importance of size effects over a wide size range, the plotted crystallization temperatures should be understood as *typical* values since, as shown in Fig. 7, other parameters of the film configuration (e.g., the Ge film thickness) have an influence on the *a*-Ge crystallization process.

For each of the multilayer films with a constant number of pulses on the Ge target, the Avrami exponent increases with increasing annealing temperature, from a value of about

FIG. 8. Schematic showing the *a*-Ge crystallization temperature variation as a function of a characteristic size for the Bi crystals in multilayer films: diameter of the NCs in this work (○), (△) (from Fig. 5), and Bi grain size [SGS (◇) and LGS (□)] in Ref. 16. For comparison, the crystallization temperature for the reference *a*-Ge film with no Bi nanocrystals $B_0G_{100}II$ (▼) is also included on the vertical axis.

2.5 at an annealing temperature close to the crystallization threshold to a value of about 5.5 at the highest annealing temperature at which quantitative analysis could be carried out. This result is obtained despite the fact that the crystallization temperature range is different for each of the films, as seen in Table II. The Avrami exponent can be partitioned:^{23,24}

$$n = a + bp,$$

where a is related to the nucleation rate, b is the dimensionality of the crystallization process, and p takes the value 1.0 for an interface-controlled process and 0.5 for a diffusion-controlled process. The linear dependence of the crystallized area on time shows that the growth is interface controlled, and therefore $p = 1.0$. The experimental results also show that the crystal growth may be approximated to a two-dimensional process ($b = 2$), since the circular crystalline Ge regions grow rapidly in size to $\sim 5 \mu\text{m}$ in diameter (see Fig. 6), which is two orders of magnitude greater than the film thickness (on the order of 20–30 nm). Two-dimensional growth results in a value $b = 2$. Hence the change in n with increasing anneal temperature arises from changes in a from 0.5 to 3.5, where $a < 1$ indicates a decreasing nucleation rate and $a > 1$ indicates an increasing nucleation rate with time. This increase in the nucleation rate when temperature increases is not surprising. It is known that *a*-Ge has a density slightly lower than crystalline Ge (*c*-Ge)²⁶ and thus crystallization will introduce stress which can further promote nucleation¹¹—the higher the temperature the greater the number of nuclei formed and thus the faster the crystallization process.

The activation energy for growth, E_g , was found to be approximately the same (1.2 eV) for all the films having Ge layers of the same thickness. This energy is lower than that reported for growth of Ge crystallites in *a*-Ge and close to that reported for *a*-Ge in contact with metals.²⁷ This result,

FIG. 9. Schematic diagram illustrating possible crystallization mechanisms: (a) initial perpendicular crystallization followed by crystallization in the plane of the layers, and (b) perpendicular crystallization only for films with thick Ge layers.

together with the fact that the crystallization proceeds in a similar way in all the films, and the identical *c*-Ge grain size found in each film, suggests that the size of the Bi NCs has no significant effect on the growth of the Ge crystallites after nucleation. A decrease of the crystallization temperature with increasing NC size means that the total activation energy decreases and the activation energy for growth remains constant, and it can then be concluded that the larger the size of the NCs, the lower the activation energy for nucleation. This result is not surprising since for the films with thinner Ge layers (thickness ≤ 5 nm) the size of the Bi NCs is large enough, and the Ge layer thickness is small enough, that the *a*-Ge cannot consist of flat layers. For these films the Ge layers are wavy, as shown schematically in Fig. 9(a). This will result in considerable strain in the *a*-Ge layers, in addition to voids and other defects, which will lower the activation energy for nucleation E_n . The extreme of this is observed for the films deposited using more than 50 laser pulses on the Bi target per layer, which contain the largest Bi NCs, in which MIC of the Ge can occur even at room temperature.

A more detailed picture of the crystallization process can be obtained when the shape of the Bi NCs and the variation with Ge layer thickness are taken into account. Previous studies of similar films²⁸ have shown the Bi NCs to be oblate ellipsoids with two major axes of similar length in the plane of the layers and a shorter axis perpendicular to the layer plane. This results in a larger surface area of Bi in contact with the Ge along the film normal direction, and hence preferential nucleation and initial growth are expected to occur along this direction.

The variation of *a*-Ge crystallization temperature with Ge layer thickness, observed for the series III films, suggests that there is a further parameter that influences the crystallization process. The crystallization temperature of the Ge is

observed to increase with increasing Ge layer thickness, up to a certain critical thickness (~ 5 nm), above which the crystallization temperature tends to a saturation value (see Fig. 7). The films in series III were each fabricated with the same number of pulses on the Bi target, and thus contain the same number of Bi atoms [see Fig. 3(a)], i.e., the Bi NCs have the same average diameter and there are the same number of NCs in each film. There is therefore the same total surface of Bi exposed to the Ge. From our earlier discussion of the MIC mechanism we would therefore expect the crystallization temperature of the Ge to be constant for all series III films. However, we observe an increase in crystallization temperature with increasing Ge layer thickness. The results in Fig. 7 suggest that the additional parameter controlling the crystal nucleation is the separation between the Bi NCs. Measurements of the separation of the Bi NCs in the film plane (made on the trilayer films) shows the average separation to be on the order of 20 nm, with this value being very similar for a range of Bi NC sizes. Since the separation of the NCs in the film-normal direction is related to the Ge layer thickness and is much smaller than that in the film plane, it is the separation in the direction perpendicular to the film plane that controls the crystallization temperature and thus the nucleation and initial growth processes. Once the separation in the normal direction approaches the critical value (around 5 nm) the crystallization temperature becomes constant. These results suggest that MIC is enhanced both by increasing the total amount of Bi in contact with the semiconductor, and by decreasing the separation of the Bi NCs below about 5 nm.

The role of NC layer separation and NC shape in the crystallization process is further supported by the two different growth patterns that have been observed. The films with thin Ge layers (series I and II and films $B_{24}G_{200}$ III and $B_{24}G_{400}$ III from series III) show a characteristic "radial growth" in the film plane with the formation of large circular crystalline regions. The films with thick Ge layers ($B_{24}G_{600}$ III and $B_{24}G_{800}$ III) in contrast show very limited crystal growth. This can be understood as a consequence of the several factors that influence the nucleation process. First, the oblate shape of the NCs results in nucleation taking place preferentially in the direction normal to the film plane. For the films with thin Ge layers, as the crystallization proceeds it quickly reaches other NCs, and thus the crystallization may proceed via a "zig-zag" mechanism, as indicated schematically by the arrows in Fig. 9(a). As we are observing this process in projection it results in the radial growth observed experimentally. For the films with thick Ge layers the process is different since the Bi crystals are further apart. When growth takes place in the film-normal direction the situation schematically shown in Fig. 9(b) occurs, and as a consequence no significant growth in the film plane is observed. The trilayers may be rationalized as the extreme of the thicker multilayer films. With only one layer of Bi NCs, the Bi NC separation in the film-normal direction is infinite and therefore the zig-zag growth model cannot apply and nucleation followed by growth has to occur in the film normal in agreement with experimental observation.

V. CONCLUSIONS

The kinetics of metal-induced crystallization of *a*-Ge in contact with Bi nanocrystals depends strongly on the size, separation, and shape of the NCs. The crystallization temperature of the Ge, and thus the activation energy for crystal nucleation, decreases rapidly with increasing Bi metal contact area, consistent with an MIC mechanism. The shape of the NCs (oblate ellipsoids) results in nucleation and initial growth of the crystalline Ge phase perpendicular to the film plane. The Bi NC separation determines the growth process: for thin Ge layers, crystal growth occurs via a zig-zag mechanism from one Bi NC to the next, with the projection of the process being radial growth in the film plane. Once the Bi NC separation in the film-normal direction increases above a critical value (~ 5 nm) crystal growth occurs mainly in the film-normal direction with only very limited growth in the film plane.

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