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Role of defects in metal mediated crystallization in Al/*a*-Ge multilayers

G. Raghavan and R. Rajaraman
Materials Science Division, Indira Gandhi Centre for Atomic Research, Kalpakkam - 603 102, India

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Metal-catalyzed crystallization of amorphous germanium (*a*-Ge) is investigated to provide experimental evidence that this phenomenon is a defect mediated process. Positron lifetime measurements are carried out on as-grown and annealed Al/*a*-Ge multilayers, to unambiguously identify the type of defects. Substantial positron trapping occurs at interfacial voids in the as-grown specimens. Annealing at temperatures of 450–533 K results in rapid interdiffusion of the layers, leading to the formation of crystalline precipitates of Ge in the Al matrix. We provide direct evidence that the rapid transport and growth of crystalline Ge precipitates is aided by the transport of defects. These defects are identified to be two/three vacancy clusters. The broader implications of these results to microstructure and phase evolution in thin film multilayers is indicated.

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Low-dimensional systems such as thin films and multilayers usually have quenched-in defect concentrations far in excess of the bulk equilibrium values. The presence of a supersaturation of point defects along with extended defects such as nanocrystalline grain boundaries drastically alter material properties such as the melting point, solid solubility limits, etc. As a direct consequence, controlled heat treatment frequently results in the production of metastable phases not accessible through bulk material processing routes. Thus, unlike in bulk systems, defects are not peripheral to issues related to phase formation and microstructural evolution but play an extremely crucial but ill-understood role. Artificially engineered thin film multilayers are far-from-equilibrium structures, which are inherently unstable under thermal perturbations. It is well established, that the phase formation sequence in annealed multilayers is governed as much by kinetics as by thermodynamics.[1] The substantial role played by defects in this interplay between thermodynamics and kinetics was spectacularly demonstrated in the phenomenon of solid state amorphization, wherein an amorphous phase forms under low-temperature heat treatment of transition metal multilayers.[2] The formation of such a patently unstable phase is known to occur only in the presence of defects.[3] Other examples on the influence of defects, now gaining recognition, are in the areas of defect mediated subcritical fluctuations during the formation of semiconductor islands[4] and in metal catalysed crystallization of amorphous semiconducting films.[5] In the latter phenomenon, the crystallization temperature of amorphous semiconductors, in intimate contact with fcc metals, is drastically reduced. This phenomenon is the inherent source of thermal instability of devices based on such structures.[5–10] Early studies on amorphous Si showed that the presence of metal contacts dramatically lowers the crystallization temperature of Si.[6] This phenomenon, referred to as metal-mediated or metal-catalyzed crystallization (MMC), has been extensively studied in Ge/metal and Si/metal systems.[5–10] While these studies emphasized the detrimental effect of MMC, Funato *et al.*[11] exploited this very effect to successfully wafer-bond GaN with Si. In yet another offshoot of MMC, Nast *et al.*[12] produced high quality polycrystalline silicon layers on glass substrate from amorphous Si/Al bilayers.

In order to understand the intriguing phenomenon of MMC, several workers have carried out careful electron microscopy investigations. It has been found that annealing of *a*-Ge/(Al, Au, Ag) films results in the rapid diffusion of Ge into the metal layer, leading to the formation of fractal-like precipitates of Ge. *In-situ* transmission electron microscopy investigations[7,10] on the growth of Ge precipitates indicate that the observed growth rates are too rapid to be explained on the basis of the diffusion rate of Ge (Ref. 13) alone. Based on this observation, Konno *et al.*[10] have conjectured that the growth of Ge precipitates in the metal layer is aided by a counter flux of vacancies. Though these studies have suggested that defects are possibly implicated in these processes, a detailed understanding and direct experimental evidence is presently lacking. Positron annihilation spectroscopy is a well established technique for probing open volume defects[14] and is hence ideally suited to address these issues. Positron based techniques have also been effectively used for characterizing early stages of precipitation in Al based alloys.[15,16] In an earlier positron annihilation Doppler broadening study on the precipitation of Ge from dilute alloys of Al-Ge, Murukami *et al.*[16] have proposed a similar vacancy mechanism for the transport of Ge. More recently one of us[17] has carried out secondary ion mass spectrometry (SIMS) and low energy positron beam measurements (LEPB) on Al/*a*-Ge bilayers. These studies demonstrated that the diffusion of Ge into the Al layer is accompanied by a sharp increase in the defect sensitive *S* parameter at the interfacial region and provided prima facie evidence that vacancylike defects are implicated in MMC. However, the analysis of Doppler broadened line shape parameters reported in these studies were of a qualitative nature only.

The present work reports positron annihilation based investigations on MMC in Al/*a*-Ge multilayers. This work has been carried out in order to understand the role played by defects in the microstructural evolution of the system. We provide conclusive evidence on the nature and source of defects involved in the MMC of Ge in Al/Ge multilayers. For these investigations, we have grown a 150 layer specimen with alternating layers of Al and Ge with a overall thickness of 30 μm and identified the type of defect and the nature of its evolution under heat treatment. Based on these measure-

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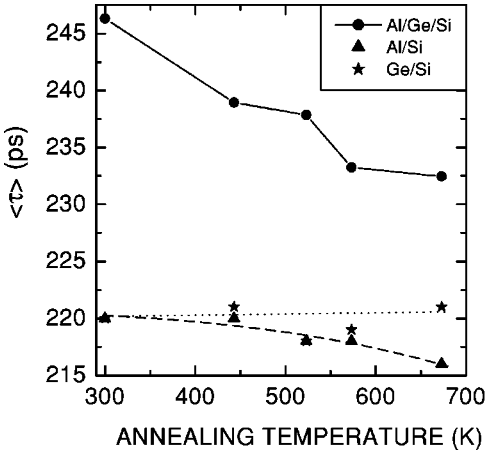

FIG. 1. Variation of mean lifetime $\langle \tau \rangle$ as a function of annealing temperature for Al single layer film, Ge single layer film, and Al/Ge multilayer film on Si. Lines are meant to guide the eye.

ments and complimentary data on intermixing and precipitation drawn from our earlier study, we propose that the growth of Ge precipitates is aided by vacancylike defects which are supplied by quenched-in interfacial voids present in the as-grown specimen.

Multilayer thin films of Al/a-Ge were deposited by electron beam evaporation at a vacuum of 3×10^{-7} mbar. The deposition and annealing chambers were preheated and degassed before use. Prior to the actual deposition of the specimens, Ti was deposited on the chamber walls to act as a getter material. Suitable precautions were also taken to minimize oxide contamination during the vacuum annealing of samples. Hundred and fifty layers, alternately of Al(200 nm) and Ge(200 nm), were deposited on a Si (111) substrate at room temperature with an overall thickness of 30 μm. Pure, single layer films of Al and Ge, each having a thickness of 30 μm were also deposited on Si (111) under identical conditions. In all the cases, the film thicknesses were measured *in situ* with a quartz microbalance, which had been calibrated, against a surface profilometer (DEKTAK 3030). Positron lifetime measurements were carried out on as-deposited specimens and after sequentially annealing these films for 2 h each at different temperatures viz. 443, 523, 573, and 663 K. The time resolution of the lifetime spectrometer used in these measurements is 225 ps (FWHM). Experimental data were analyzed for multiple lifetime components using POSITRONFIT and RESOLUTION programs.[18]

Multilayer thin film specimens with N layers have N internal interfaces including the one between the substrate and the film. These internal surfaces are potential sources of defects and hence we expect the positron annihilation characteristics of the multilayer film to be different from that of the single layer films of the same nominal thickness. In order to investigate these differences, positron lifetime measurements were carried out on (i) the bare Si substrate, (ii) single layer film of Al (30 μm) on Si, (iii) single layer film of Ge (30 μm) on Si, and (iv) Al/a-Ge multilayers on Si. Figure 1 shows the variation of mean positron lifetime as a function of annealing temperature for single and multilayer films. The lifetime for the Al and Ge films were 220 and 221 ps, respectively, which are close to that of bulk Si. Further, these values did not change much even when the films were annealed at 673 K for 2 h. This observation can be understood by considering the range of positrons in these samples. The range R can be computed using the expression[19]

$$R(\mathrm{cm}) = \frac{1}{17} \times \frac{E_{\max}^{1.43}(\mathrm{MeV})}{\rho(\mathrm{g/cm}^3)}, \tag{1}$$

where ρ is the density of sample and $E_{\max}$ is the maximum positron energy corresponding to the positron source (540 keV for ^{22}Na). The mean range of positrons in Al and Ge are estimated to be 90 and 46 μm, respectively. For 30 μm thick films, $\sim$30 and 50 % of positrons are expected to probe Al and Ge films, respectively. Hence, in the absence of any defects, the mean lifetime in Al/Si should be $\sim$203 ps and that of Ge/Si will be $\sim$225 ps. The higher mean lifetime for Al/Si sample than the expected value of 203 ps indicates that there are defects in as deposited sample. However, only one lifetime component could be resolved in single layered Al/Si and Ge/Si samples. This may be due to the lifetime ratio of film and substrate being <1.5, which is the resolving limit of the positron technique[20] and the defect concentration being smaller than the detectable limit. The slight reduction seen in mean lifetime for Al/Si sample with annealing temperature indicates that defects are indeed annealing out. As the fraction of positrons probing the single interface is negligible due to the mean positron diffusion length of few hundred nanometers,[20] very little trapping is expected from the film/substrate interface. These facts indicate, that most of the positrons are getting annihilated in the bulk, comprising of film and substrate. This however is not the case for the multilayer specimen of an identical nominal thickness. As seen from Fig. 1, The mean lifetime for as-deposited multilayer film is 245 ps. It decreases with annealing temperature and a shoulder is seen around 523 K. Interestingly the mean lifetime does not reach the bulklike value even at the last annealing step of 673 K.

In order to have a better understanding of these results, lifetime spectra corresponding to Al/a-Ge multilayer film were analyzed for multiple components. A good fit could be obtained with no more than two lifetime components. Inclusion of an additional component always resulted in unphysical values. Figure 2 shows the variation of resolved lifetime components τ_1, τ_2, and I_2. The resolved intensity I_1 corresponding to τ_1 is not shown, since $I_1=(100-I_2)$. For the as grown multilayer, the τ_1 component is 218 ps which arises from the bulk state of both the multilayer film and the Si substrate. The τ_2 component has a value of 416 ps. This value is much larger than the bulk lifetime for Al (166 ps),[21] Ge (230 ps),[22] and that of the Si substrate (218 ps). The intensity of this component is 14%, indicating that a sizable fraction of the positrons is getting annihilated in the multilayer film. Since very little positron trapping occurs in the single layer specimens, we conclude that the τ_2 component arises due to positron trapping at the large number internal Al/Ge interfaces present in the multilayer film. This lifetime component is fairly close to that obtained for microvoids composed of large vacancy clusters in Al (Ref. 21) or

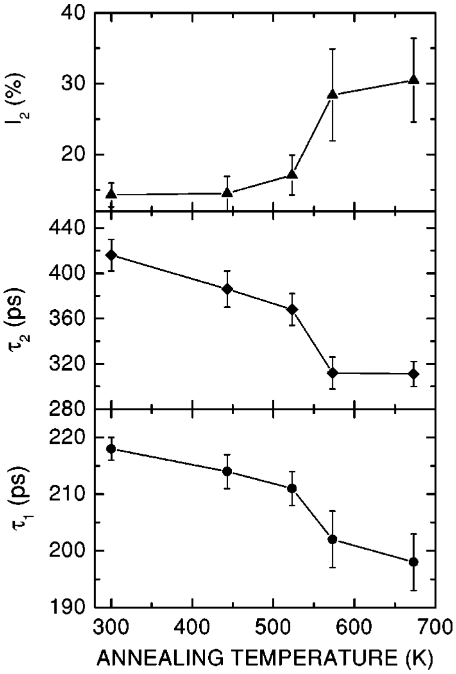

FIG. 2. Variation of resolved lifetime components as a function of annealing temperature for Al/Ge multilayer film on Si. Lines are meant to guide the eye.

Ge.[22] This observation, coupled with the fact that there is negligible positron trapping in the single layer films, leads us to ascribe the 416 ps component to voids present at each of the interfaces between the Al/Ge layers. This is understandable as there are 150 interfaces including the substrate/film interface. The assertion that the 416 ps component comes from interfacial voids is further justified by the following considerations: (i) Assuming a mean density for the multilayer film to be ~ 4 g/cm^3, the range R of positron is calculated using Eq. (1) to be 60 μm, whereas the overall multilayer thickness is only 30 μm. Hence, in the absence of defects at interfaces, very little positron trapping would occur and positrons would see only the bulk states of the film and substrate. (ii) Since the typical diffusion length of positrons is of the order of a few hundred nanometers in defect free materials,[20] most of the positron stopped within the 30 μm thick multilayer has a high probability of sampling all the interfaces as each layer thickness is only 200 nm. (iii) It may be emphasized that the underlying microstructure cannot give rise to the observed differences in the positron annihilation characteristics between the thick single layer films and the multilayer specimen. It is well known that crystalline Ge films can be grown only by high temperature deposition. Thus, Ge films deposited at room temperature are amorphous irrespective of thickness.[17] Aluminum films deposited at room temperature are nanocrystalline with the average grain size being more or less constant for films thicker than 100 nm. Thus, we believe that the differences between the single layer and multilayer specimens cannot be attributed to the microstructure. The absence of the large lifetime component in the single layer films clearly rules out the possibility of voids being present in the bulklike regions of the multilayers. This would imply that the 416 ps component arises from interfacial voids present at the incoherent interfaces between the Al and Ge layers. (iv) The lifetime component τ_1 (218 ps), is slightly smaller than τ_b of single layer films with Si substrate (221 ps). Such a reduction in τ_b is expected in a two state trapping model when τ_2 is associated with defects and τ_1 to the bulk component τ_b and trapping rate. Thus, it is clear that the lifetime components are correctly assigned. In an earlier report on depth resolved investigations of Al/Ge bilayers,[17] it was shown that the normalized S-parameter peaks at the interface region, clearly indicating the presence of localized defects. However, it should be noticed that the nature of defect cannot be conclusively identified by mere S-parameter results. Earlier investigations on Si/Ge/Si trilayer[23] and W/Si (Ref. 24) interfaces, using depth resolved positron beam technique, indicate that a substantial positron trapping occurs at the interface region. Apart from the enhanced defect concentrations, a positive charge state of defects in Ge as well internal electric field at the interface[24] would be reasons for the substantial field-induced drift and subsequent trapping of positrons at interfacial defects. Thus, it is not surprising that unlike the case of the single layer films, a significant fraction of positrons are trapped at interfacial defects which are identified to be voids in the present study.

The evolution of defects along with interdiffusion of Al and Ge during annealing is clearly seen from Fig. 2. The larger component τ_2, is seen to have decreased from 416 to 386 ps upon 443 K annealing for 2 h. Calculated lifetime values for 6 and 13 vacancy clusters in Al are 351 and 422 ps, respectively.[21] Hence, the fall in τ_2 value indicates that interfacial voids are shrinking in size by emitting vacancies. Compositional depth profiling on Al/Ge bilayers using SIMS[17] indicates the onset of interdiffusion between the layers at this stage of heat treatment. Interfacial mixing is, however, only marginal. There is, however, a substantial rearrangement in the vicinity of the interface due to localized transport of atoms. Such a mobility of the atoms appears to be accompanied by the emission of vacancies from the interfacial voids. These vacancies are presumably annihilated at local sinks and as a result we see a reduction in void size with only a marginal increase in vacancy concentration. This interpretation is consistent with the observed reduction in τ_2 accompanied by only a small change in I_2. The trends in τ_1, τ_2, and I_2 is similar after the next stage of anneal at 523 K as well. The 368 component, observed at this temperature, is also fairly close to that for six-vacancy clusters. Once again we find a small increase in I_2. The next stage of annealing at 573 K, however, results in interesting changes. At this point, we see a marked change in the behavior of τ_1, τ_2, and I_2. The lifetime components τ_2 and τ_1 fall off abruptly at this stage. It is found that τ_2 drops from 368 to 312 ps and I_2 increases from 17 to 28 %. The defect component is consistent with known values of di/trivacany clusters in Al.[21] SIMS depth profiles[17] on Al/Ge bilayers show that there is a complete intermixing in the sample following this annealing stage. For the purpose of carrying out transmission electron microscopic (TEM) studies, we have specially prepared Al/a-Ge bilayer specimens of 50 nm / 50 nm thickness. This dimension is chosen for the purpose of electron transparency.

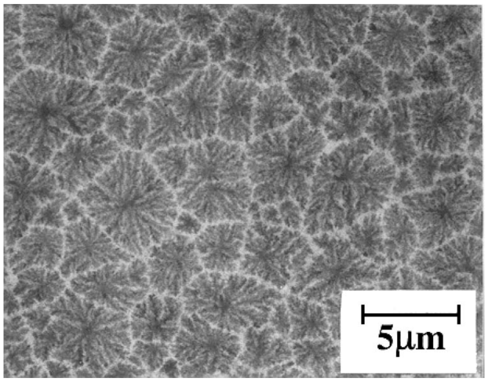

FIG. 3. Typical TEM bright field image of fractal-like Ge precipitates in Al(50 nm) / *a*-Ge (50 nm) bilayer film annealed at 500 K for 30 min. The image is representative of precipitates undergoing rapid defect mediated growth.

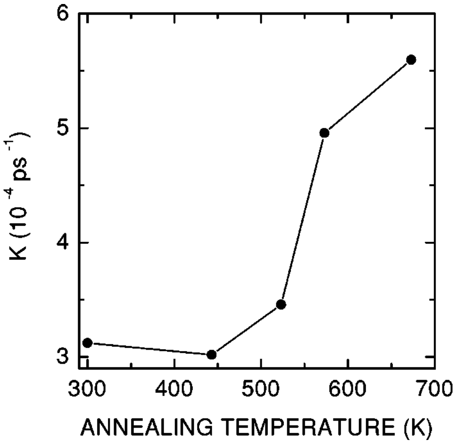

FIG. 4. Variation of total trapping rate, estimated using resolved lifetime components as a function of annealing temperature for Al/Ge multilayer film on Si. Lines are meant to guide the eye.

Figure 3 shows a typical TEM bright field image of fractal-like Ge precipitates in bilayer film annealed at 500 K for 30 min. Since the morphology of precipitates is fairly independent of thickness, this image is representative of precipitates undergoing rapid defect mediated growth. Thus, it is seen that interdiffusion is accompanied by huge increase in the concentration of such vacancy clusters which accelerates the growth of fractal-like precipitates. This observation is also borne out clearly by the huge increase in the trapping rate computed from the two state trapping model, as shown in Fig. 4. It should be noted at this stage that there is no signature of the interfacial void that was present prior to the anneal. Thus, the process of interdiffusion not only smears out the interfaces but also results in the breaking up of the voids into a large number of small vacancy clusters. This sequence of events appears to be the only plausible explanation, which is consistent with the observed reduction in τ_2 accompanied by a large increase in I_2. Murukami *et al.*[16] have proposed that a single vacancy could mediate the exchange of one or more Ge atoms during their precipitation from a dilute alloy. From their Doppler broadening studies, it was argued that Ge atoms decorate vacancy clusters in such precipitates. All these observations are consistent with and strengthen the experimental results obtained in the present work. The changes occurring after the final stage of annealing at 673 K are only marginal. These changes in annihilation characteristics are consistent with an observation of a complete precipitation of Ge from the matrix.[17] Hence, our present results have provided experimental evidence for the predominant role of vacancylike defects in metal mediated crystallization. As in the case of Al-Ge, the equilibrium phase diagram of most MMC systems are simple eutectic with extremely poor mutual solid solubilities of the components and hence we expect that the conclusions drawn from the present study would be of a generic validity.

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