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Temperature dependence of compositional disordering of GaAs-AlAs superlattices during MeV Kr irradiation

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The influence of the specimen temperature during MeV Kr irradiation on the extent of compositional disordering in GaAs-AlAs superlattices has been determined. For low-temperature irradiations (133–233 K), complete intermixing of the superlattice is observed. However, the mixing efficiency *decreases* with increasing specimen temperature between room temperature and 523 K. These results suggest the existence of a miscibility gap in the coherent-phase diagram of GaAs-AlAs superlattices with a critical temperature greater than 523 K.

Compositional disordering of III-V compound semiconductor epitaxial structures has great promise for the microfabrication of unique optical and electronic devices. One of the requirements for device fabrication is that the disordering be achieved selectively. Impurity-induced compositional disordering using Zn or Si diffusion or conventional ion implantation is often employed[1–3] for this purpose. However, in some cases, the incorporation of such electrically active impurities is undesirable.[4] Ion-beam mixing provides an alternative means for inducing selective compositional disordering, not limited to active impurities. Important considerations for ion-beam mixing are the damage the irradiation introduces into the sample, the ability to anneal such damage, and the efficiency with which the superlattice can be disordered. An important parameter for all three of these concerns is the sample temperature during the mixing irradiation.[5] This work focuses on the influence of sample temperature on the mixing efficiency. We will show the unexpected result that the mixing efficiency decreases with increasing substrate temperature between room temperature and 523 K, the highest temperature employed in this work. The implication of this observation is the existence of a miscibility gap in the coherent-phase diagram of the GaAs-AlAs superlattice system (wavelength ~400 Å) with a critical temperature greater than 523 K.

The technical implications of ion-beam mixing for the fabrication of thin-film devices and for surface treatments have been recognized[6] for several years, and a basic understanding of the physical processes underlying ion-beam mixing are beginning[7–9] to emerge. Two regimes are distinguishable[5,8–10] in the temperature dependence of ion-beam mixing. At lower temperatures, mixing is nearly independent of temperature and the system can be driven far from thermodynamic equilibrium. At higher temperatures, mixing is strongly (exponentially) dependent on temperature and the system moves toward equilibrium.

Ion-beam mixing in the low-temperature regime derives from the atomic rearrangement which occurs during the evolution of energetic displacement cascades. Early in the cascade evolution, atoms are displaced from their lattice sites by collisions with energies greater than ~5 eV. Later, when the initial recoil energy becomes partitioned among all atoms in the volume of the cascade, a thermal spike condition develops and diffusion takes place within the hot spike. Although questions about thermal spike dynamics remain, it is recognized[5,7,8] that atomic motion occurs while the atoms are highly excited, with atomic energies on the order of 1 eV. It is because the atomic rearrangements occur with such high energies relative to the ambient lattice temperature that a system can be driven far from equilibrium. In addition to creating atomic disorder, displacement cascades also produce point defects, i.e., vacancies and interstitial atoms. At elevated lattice temperatures, these defects are mobile and cause atomic diffusion, usually called radiation-enhanced diffusion. Since this diffusion process takes place long after the thermal spike has cooled and extends well beyond the original boundaries of the displacement event, radiation-enhanced diffusion tends to return the system to equilibrium. Although cascade mixing and radiation-enhanced diffusion both occur during high-temperature irradiations, the latter dominates at sufficiently high temperatures.[10] The transition between low- and high-temperature mixing occurs in the temperature range where both vacancies and interstitials become mobile, above room temperature in most cases. The experiments described here were undertaken to determine the transition-temperature range and to explore whether radiation-enhanced diffusion could be employed to enhance the disordering efficiency of the superlattice.

The samples used for these experiments were GaAs-AlAs superlattice (SL) structures grown[11] by atmospheric pressure metalorganic chemical vapor deposition at 800 °C. The substrates are (100)GaAs doped with silicon to a carrier concentration of 2×10^{18} cm^{-3}. The epitaxial structure consists of a 0.25-μm GaAs undoped buffer layer and a 50-period undoped SL of alternating layers of 200-Å GaAs and 200-Å AlAs. As a consequence of the growth temperature, the superlattice has a background *p*-

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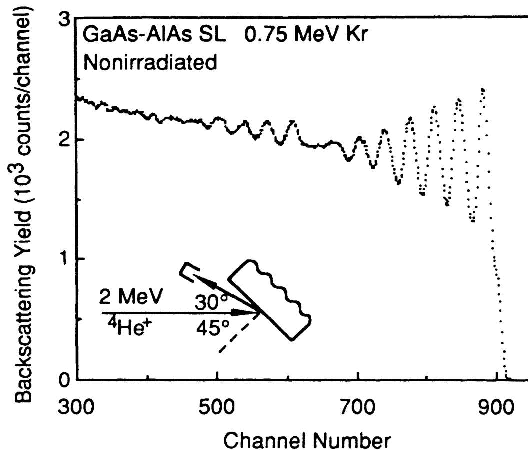

FIG. 1. Rutherford backscattering spectrometry spectrum of the GaAs-AlAs superlattice sample prior to irradiation. A schematic of the sample geometry employed for the relatively high resolution Rutherford backscattering spectrometry is shown in the inset.

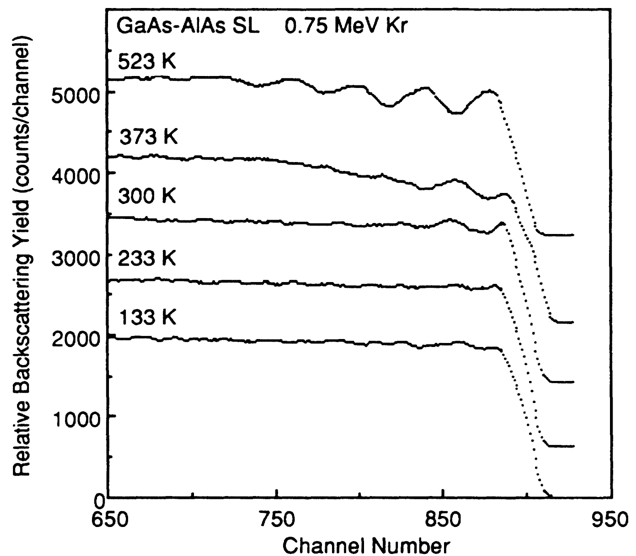

FIG. 2. Rutherford backscattering spectrometry spectra showing the extent of ion-beam mixing in GaAs-AlAs superlattices following 0.75-MeV Kr^+ irradiation (2×10^{16} cm^{-2} dose) at several specimen temperatures.

type carrier concentration of $\sim 1\times10^{18}$ cm^{-3}. The specimens were irradiated with 0.75-MeV Kr^+ at the Van de Graaff accelerator facility at the Materials Research Laboratory at the University of Illinois. The ion-beam current on the sample was kept constant at 120 nA for each irradiation. The beam was wobbled over an aperture plate to provide homogeneity on the 0.1-cm^2 test spots scribed on the sample. The background pressure in the irradiation chamber was below 6×10^{-8} Torr for all irradiations. The extent of intermixing of the SL layers was determined in all samples by Rutherford backscattering spectrometry (RBS) using 2-MeV He^+ and checked in selected cases by secondary-ion mass spectroscopy (SIMS). All specimens were analyzed at room temperature. The range of the 0.75-MeV Kr^+ in GaAs is $\sim$0.3 μm, and since only the first six periods of the SL could be used for RBS analysis, the effect of implanted Kr and gradients in the damage distribution can be neglected. The influence of the damage distribution on mixing at greater depths, however, was observed in the SIMS measurements.

A typical Rutherford backscattering spectrum of the GaAs-AlAs SL sample collected before irradiation is illustrated in Fig. 1. The backscattering geometry is shown in the inset. The oscillations in the yield at high energies for the nonirradiated sample derive from the superposition of the Ga and As yields in the SL. The Al yield occurs at lower energies, channels 475–625 in the spectra, where additional oscillations are seen. The attenuation of these oscillations is a consequence of the loss of resolution with depth arising from straggling and lateral spread of the analysis beam.[12] The relatively rapid loss of resolution with depth is due to the high-resolution geometry.[13] Rutherford backscattering spectra of the irradiated GaAs-AlAs SL samples are shown in Fig. 2. The Kr^+ irradiation fluence was 2×10^{16} cm^{-2} for all temperatures. The spectra indicate that below room temperature, the SL becomes completely disordered by the Kr irradiation. At room temperature, some oscillatory structure is maintained, and at increasingly higher temperatures, the amplitude of the oscillations increases. At 523 K, the amount of disordering is far less than at low temperatures, although evidence for partial disordering is still clearly visible.

The Al concentration obtained by SIMS as a function of depth are illustrated in Fig. 3 for the nonirradiated sample and samples irradiated at 133 and 523 K. Al-

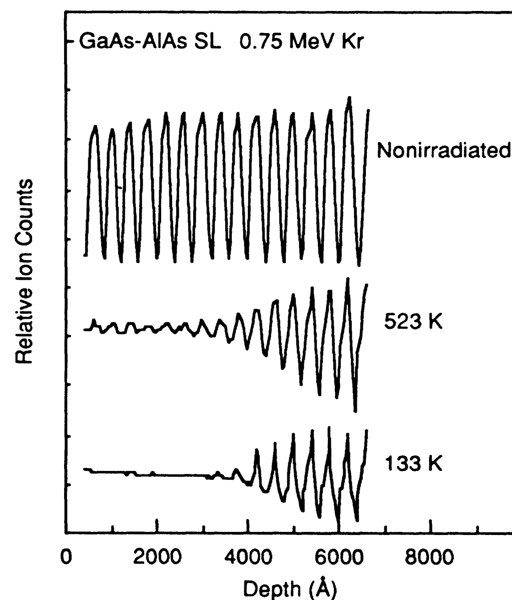

FIG. 3. Secondary-ion mass spectrometry depth profiles of ^{27}Al for GaAs-AlAs SL samples prior to irradiation and following 0.75-MeV Kr^+ irradiation (2×10^{16}-cm^{-2} dose) at 523 and 133 K.

though SIMS cannot be employed for quantitative compositional analysis, it does reveal the interdiffusion quite clearly. The specimen irradiated at low temperatures shows complete disordering from the surface to approximately the mean projected range of the Kr ions, 320 nm. At this position the deposited damage energy density decreases rapidly with depth.[14] The interdiffusion in the specimen irradiated at 523 K, however, shows only partial intermixing, with no obvious dependence on depth until the end of the Kr-ion range. Since the deposited damage energy varies only by ~30% between the surface and 300 nm, it is uncertain whether the depth-independent disordering is an indication that the interdiffusion has saturated at this fluence.

The temperature dependence of compositional disordering found here is similar[15] to that observed previously during ion-beam mixing of Cu-Nb and Cu-Bi diffusion couples. In those cases, interdiffusion was observed at low temperatures where point defects are immobile, but was strongly reduced at room temperature. These alloy systems have limited solid solubility but are completely miscible as liquids; thus, the explanation for their mixing behavior follows directly from application of the Darken expression for chemical interdiffusion, i.e.,

$$\tilde{D}(N_A) = (D_A N_B + D_B N_A) \frac{x_A x_B}{RT} \frac{\partial^2 G}{\partial x^2}, \quad (1)$$

where $\tilde{D}(N_A)$ is the chemical interdiffusion coefficient in the alloy with concentration N_A, D_i is the tracer diffusion coefficient of element i in the alloy, x_i is the mole fraction of element i, R is the gas constant, T is the temperature, and G is the molar free energy of the alloy. The second factor on the right-hand side in Eq. (1) is the thermodynamic factor which reduces to $1-2\Delta H_{mix}/k_B T$ in the regular solution approximation. It is immediately obvious from this latter expression that during the cascade, when the effective temperature is far in excess of the melting temperature, thermodynamics can play only a minor role (note T in the denominator). For GaAs-AlAs, like Cu-Bi and Cu-Nb, the heat of mixing is positive but much less than an electron volt[16] so that the thermodynamic factor reduces to unity. Therefore, at low temperatures the chemical interdiffusion coefficient is positive and disordering is observed.

At high temperatures, the mixing due to radiation-enhanced diffusion (RED) must be added to that due to cascade mixing,

$$D(T) = D_{cascade} + D(T)_{RED}. \quad (2)$$

Application of Eq. (1) to $D(T)_{RED}$ reveals a far greater sensitivity to the thermodynamic factor since the temperature here corresponds to the ambient-specimen temperature and not the thermal-spike temperature. Thus, at high specimen temperatures, the thermodynamic properties of the system strongly influence the diffusion behavior. Since it is observed that cascade mixing is sufficient to completely disorder the superlattice, as demonstrated by the low-temperature irradiations, the incomplete disordering at 523 K indicates that the radiation-enhanced diffusion coefficient must be negative at that temperature, i.e., $\partial^2 G/\partial x^2 < 0$. Since the GaAs-AlAs SL system intermixes completely by thermal diffusion above ~1250 K, our observations suggest the presence of a miscibility gap in the phase diagram of this system. It has been recently reported[17] that GaAs-AlAs SL's compositionally disorder during Ne irradiation at 973 K. Thus, the critical temperature of the miscibility gap must lie between 523 and 973 K. If the magnitude of $D(T)_{RED}$ becomes greater than $(D_{cascade})$ at a temperature below the critical temperature, the compositional depth profile should become stable against further disordering. It is unlikely, however, that the SL will perfectly maintain its one-dimensional compositional profile in such a case. Demixing $[D(T)_{RED}]$ occurs after the mixing $(D_{cascade})$ and so roughening of the planar interface is likely to occur, making it difficult to observe this stability by RBS or SIMS. Nevertheless, by finding the stable-composition profiles as a function of temperature, it becomes possible to experimentally determine the coherent spinodal of the GaAs-AlAs SL.[10] Further investigation of the dose dependence, the critical temperature of the miscibility gap, and other features of the phase diagram are presently in progress.

The existence of a miscibility gap in the GaAs-AlAs system has been the subject of several theoretical investigations, with one predicting no miscibility gap[18] and others finding critical temperatures ranging[19-21] between 59 and 400 K. To our knowledge, experimental observation of a miscibility gap in bulk $Al_xGa_{1-x}As$ or GaAs-AlAs SL has not been reported prior to this study. Presumably, this is because the critical temperature of the miscibility gap is below 973 K and diffusion at these temperatures is negligible. Only by enhancing diffusion by irradiation could the low-temperature region of the phase diagram be explored.

Implicit in the above discussion is the assumption that $D_{cascade}$ is independent of temperature. For semiconductor systems like the GaAs-AlAs SL studied here, irradiation often induces an amorphous phase at low temperatures but not at temperatures where RED is important. GaAs is known to behave in this manner.[22] We cannot exclude the possibility, therefore, that the reduced mixing at elevated temperatures is due to $D_{cascade}$ being greater in the amorphous structure (low-temperature irradiation) than in the crystalline phase (high-temperature irradiation). Our preliminary results on the dose dependence of mixing indicate that $D_{cascade}$ would need to be a factor of 10 larger in the amorphous phase than in the crystalline phase; the authors, however, are not aware of any system, metallic or semiconductor, where $D_{cascade}$ has been shown to decrease with increasing temperature, regardless of phase transitions. Moreover, Pearton *et al.* implanted Sn into GaAs at 77, 293, 473, and 673 K and found that the Sn profile was sharpest for 77-K implantation and became successively broader with increasing implantation temperature.[22] Thus, the decrease in the GaAs-AlAs SL disordering rate with increasing temperature observed here is unlikely to result from anomalous behavior in $D_{cascade}$, but rather it appears to be a consequence of thermodynamics as outlined above.

In summary we have examined the influence of the

sample temperature during MeV Kr irradiation on the extent of compositional disordering in GaAs-AlAs superlattices. The superlattice is observed to completely intermix during low-temperature irradiations. The mixing efficiency, however, decreases with increasing sample temperature between room temperature and 523 K. These results suggest the existence of a miscibility gap extending to temperatures above 523 K in the GaAs-AlAs superlattice phase diagram.

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