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Pulsed electron beam induced recrystallization and damage in GaAs

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Single-pulse electron-beam irradiations of 300-keV $10^{15}Kr^+/cm^2$ or 300-keV 3×10^{12} Se^+/cm^2 implanted layers in unencapsulated ⟨100⟩ GaAs are studied as a function of the electron beam fluence. The electron beam pulse had a mean electron energy of $\simeq$20 keV and a time duration of $\simeq10^{-7}$ s. Analyses by means of MeV He^+ channeling and TEM show the existence of narrow fluence window (0.4–0.7 J/cm^2) within which amorphous layers can be sucessfully recrystallized, presumably in the liquid phase regime. Too high a fluence produces extensive deep damage and loss of As.

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Thermal annealing of GaAs to remove heavy ion implantation damage and to electrically activate dopants is typically done at temperatures $\geqslant$800 °C. In order to prevent escape of As and precipitation of Ga, the GaAs surface must be protected by an inert encapsulant such as Si_3N_4 or SiO_2. However, no one encapsulant is suitable for all processes.[1] Another approach is to provide a suitable ambient pressure of As and Ga during annealing, but this method has not yet been fully optimized.[2] An attractive alternative is to use transient annealing as in the case of Si.[3] Several recent studies[4–7] have indicated that laser annealing can indeed be used for removing damage in implanted amorphous GaAs layers and for placing the implanted species into substitutional sites. The use of a pulsed electron beam to achieve comparable results has recently been reported.[8] For a 300-keV, 10^{15} Se^+/cm^2 implantation, the measured free electron concentration achieved by transient annealing was higher than that obtained after furnace annealing, but the mobility was lower. Low dose ($<10^{14}$ Se^+/cm^2) implantations, however, did not show any measurable electrical activity after transient annealing. This letter compares the results of pulsed electron beam irradition of high dose and low dose implanted layers in GaAs. The layers were characterized by He^+ Rutherford backscattering/channeling spectrometry and transmission electron microscopy (TEM).

Semi-insulating Cr-doped GaAs wafers of ⟨100⟩ orientation were implanted at room temperature with 300-keV Kr^+ ions to a (high) dose of 10^{15} cm^{-2}, or with 300-keV Se^+ ions to a (low) dose of 3×10^{12} cm^{-2}. The ⟨100⟩ axis of the wafers was offset by $\sim7°$ with respect to the beam during implantation. The unencapsulated wafers were cleaved into several samples which were each irradiated with a single electron beam pulse in vacuum (Spire Corp., Bedford, MA 01730). The mean electron energy was $\sim$20 keV, and the pulse duration was $\sim10^{-7}$ s.[9] Channeling measurements were taken by using a 2.4-MeV He^+ beam incident on samples over areas typically 1×2 mm. TEM studies were performed on the same samples in "plan" view.

Results of channeling and TEM analysis are given in Figs. 1 and 2. The unirradiated high dose Kr^+ implanted sample had a 2200-Å-thick amorphous surface layer [Fig. 1(a)]. The As/Ga ratio at the surface, obtained from the random backscattering spectrum, was close to unity. TEM plan view showed the damage as a featureless structure [Fig.

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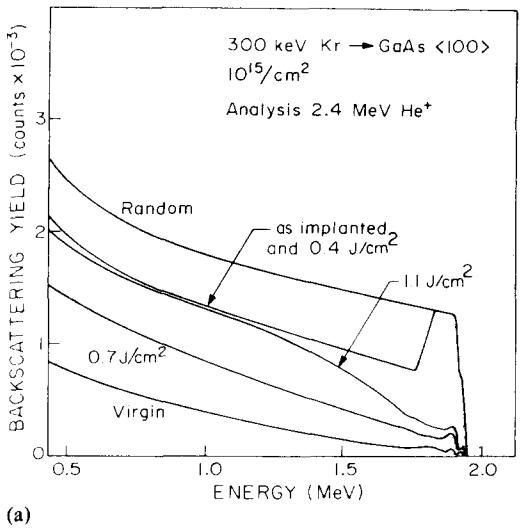
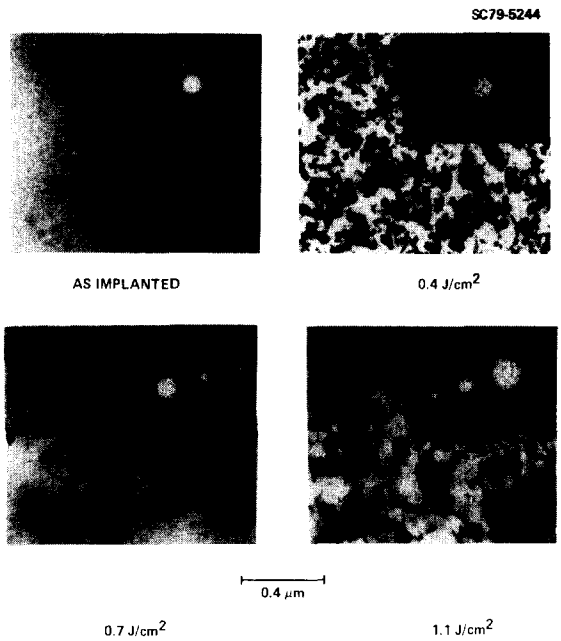


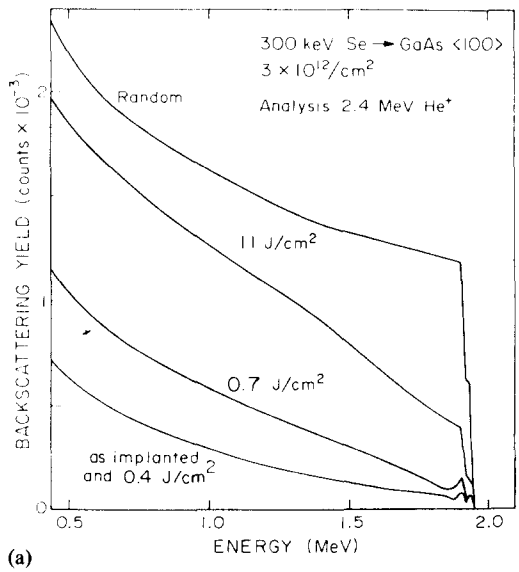
(a)



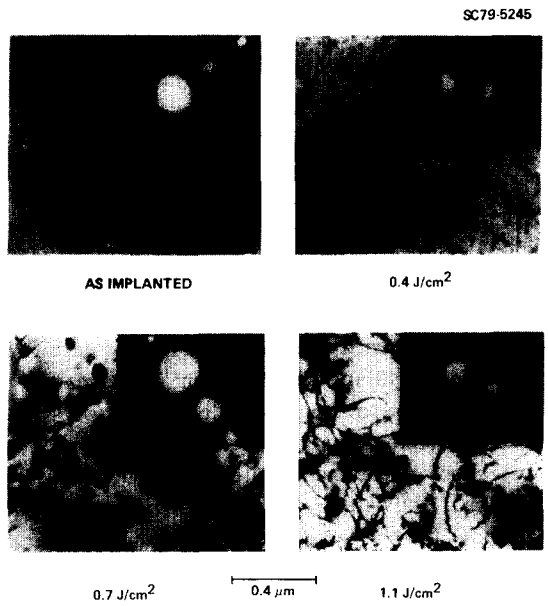
(b)

FIG. 1. (a) Energy spectra of 2.4-MeV ^{4}He$^+$ ions backscattered from ⟨100⟩ GaAs, implanted at room temperature with 300-keV 10^{15} Kr$^+$/cm^2, before and after single-pulse electron beam irradiations at the indicated fluences. The random spectrum is for the as-implanted (unirradiated) sample. The aligned spectrum from a virgin sample (unimplanted and unirradiated) is shown for comparison. The Kr signal is too small to be observed in all cases. (b) TEM micrographs for the same samples as in (a).

1(b)], and the transmission electron diffraction (TED) pattern confirmed the existence of the amorphous layer [Fig. 1(b)]. After a pulsed electron irradiation of 0.4 J/cm^2, the aligned spectrum was the same as before irradiation [Fig. 1(a)]. However, TEM results showed that the layer now had a grainy structure with mean grain size ~1000 Å [Fig. 1(b)]. The TED pattern indicated the existence of a polycrystalline layer [Fig. 1(b)]. After a 0.7-J/cm^2 irradiation, the channeling yield at the surface, χ_0, had dropped from 1.00 to 0.11 [Fig. 1(a)], indicating rather good crystalline quality. Comparison with the aligned spectrum for a virgin crystal (i.e., unimplanted and unirradiated), for which $\chi_0 = 0.04$ in the setup used in this work, showed that some disorder was present after a 0.7-J/cm^2 pulse. The surface of the irradiated sample was found to be Ga rich (As/Ga≃0.8). TEM [Fig. 1(b)] indicated the existence of dislocation lines and gray patches in the regrown layer. TED indicated that the layer was now a single crystal [Fig. 1(b)]. At a still higher electron fluence of 1.1 J/cm^2, the surface channeling yield was 0.17,



(a)



(b)

FIG. 2. (a) Energy spectra of 2.4-MeV ^{4}He$^+$ ions backscattered from ⟨100⟩ GaAs, implanted at room temperature with 300 keV, 3×10^{12} Se$^+$/cm^2, before and after single-pulse electron beam irradiations at the indicated fluences. The random spectrum is for the as-implanted (unirradiated) sample. The spectrum for a virgin sample (unimplanted and unirradiated) cannot be distinguished from the one for the as-implanted sample on this scale. The Se signal is too small to be observed in all cases. (b) TEM micrographs for the same samples as in (a).

and a high dechanneling rate indicated the presence of extended defects down to a depth greater than 1 μm [Fig. 1(a)]. The As/Ga ratio at the surface was $\simeq$0.8. TEM showed a high density of dislocations and the presence of microcracks [Fig. 1(b)]. TED indicated the material was still a single crystal. To summarize the observations of electron beam pulsed annealing of high dose (10^{15} cm^{-2}) Kr^+ implanted GaAs, it was noted that at low energy density (0.4 J/cm^2), the recrystallization of the amorphous layer gave rise to the formation of polycrystalline material. Electron irradiation pulsing of 0.7 J/cm^2 or higher resulted in single crystalline layers with increasingly higher density of dislocations. The optimum energy density for successful recrystallization seems to lie between 0.4 and 0.7 J/cm^2 for the pulsed electron beam parameters chosen.

Figure 2 shows the results of measurements performed on the low dose (3×10^{12} cm^{-2}) Se^+ implanted and pulsed electron beam irradiated samples. Both the unirradiated and the 0.4-J/cm^2 irradiated samples exhibited a χ_0 value of 0.05, almost as good as a perfect single crystal [Fig. 2(a)]. The surface composition was stoichiometric. However, TEM examination [Fig. 2(b)] of the 0.4-J/cm^2 irradiated sample revealed the existence of disordered zones (gray patches) with some probable Ga precipitates (black dots).[10] After a 0.7-J/cm^2 pulse irradiation, χ_0 increased to 0.07, the channeled spectrum was found to be well above that for the unirradiated sample, and the surface As/Ga ratio was 0.75. TEM analysis [Fig. 2(b)] revealed Ga-rich regions (black patches and dots) and the irradiated layer was found to possess dislocation lines and stacking faults. TED showed that the layer was still single crystalline. At an electron fluence of 1.1 J/cm^2, χ_0 reached 0.31 [Fig. 2(a)], and the shape of the channeled spectrum indicated a heavily disordered structure. The As/Ga ratio at the surface was $\simeq$0.7. A TEM micrograph for this sample [Fig. 2(b)] exhibited a dense dislocation network, probably arising from high thermal stresses produced by rapid temperature change.

In summary, the recrystallization and annealing of implanted GaAs layers by a pulsed electron beam can be interpreted as occurring via liquid phase regrowth. A first evidence is by the existence of a threshold for the annealing of amorphous layers. For the electron beam parameters chosen, the annealing threshold lies between 0.4 and 0.7 J/cm^2 for a 2200-Å amorphous layer created by a room temperature 300-keV 10^{15} cm^{-2} Kr^+ implantation. Below the threshold, at 0.4 J/cm^2, it appears that the electron beam pulse induces melting of the amorphous layer, but the melt depth does not penetrate the entire 2200 Å of the amorphous layer, thus leading to polycrystalline regrowth on an underlying heavily damaged layer. Above the threshold, melting of the entire amorphous layer takes place, leading to epitaxial regrowth on single crystalline substrate. These observations are in agreement with analogous studies performed on laser-annealed samples.[11–13] Crystalline (or slightly damaged) layers irradiated wth an electron beam pulse of 0.4 J/cm^2 or higher possess lattice defects, and no measurable electrical activation of the implanted species (3×10^{12} Se^+/cm^2 in the present case) is observed, in contrast to capped thermal annealing where good activation ($\geqslant$60%) is achieved.[14] It is interesting to note that electron beam pulsing at a fluence of 0.7 J/cm^2 produces more damage in the high dose amorphous implanted layer than in the low dose case, as seen in the respective channeling spectra. This effect can be explained as follows. The absorption of energy deposited by the electron beam is not expected to depend significantly on the microstructure of the material. However, the thermal properties of the layers, namely, the latent heat of fusion and the melting temperature, which control the melt depth and the duration for which the layer remains molten, may be different in the two cases. A similar dependence for electron beam irradiation of implanted layers in Si has been previously observed.[15] Amorphous or heavily damaged layers would have a lower heat of fusion than crystalline material. Thus, for equal electron beam fluence, an amorphous layer would melt deeper and stay molten longer than a crystalline layer. Observations indicate a significant loss of As at the surface after a 0.7 J/cm^2 pulse irradiation. Thus, as already pointed out by Tsu *et al.*,[7] the regrowth would take place from a Ga-rich liquid, which may account for some of the disorder. These effects are even more pronounced for 1.1-J/cm^2 irradiations. It would appear that a judicious choice of electron beam parameters (such as fluence, pulse length, and energy distribution) could be found which would optimize the annealing process in GaAs.

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Thin film characterization by atom probe field ion microscopy

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We have demonstrated that the atom probe field ion microscope (APFIM), with its resolution and single atom detection capability, is a potentially valuable thin-film characterization tool for both structural and compositional analysis. APFIM results for a range of thin films deposited onto Mo FIM tips by rf sputtering show details of void network structures, local ordering in amorphous materials, and atomic clustering effects. For instance, large ($\sim$100–300 Å diameter) isolated voids are seen in WO_3 and Ge films while smaller ($\sim$10–100 Å) interconnected voids appear in the metallic films investigated (Ni, Pt, Au). Layer-by-layer depth profiling of atomic structure and selected area (10–30 Å diameter) compositional analysis for each layer are possible by pulse evaporation. From these latter experiments the existence of ion clusters is clearly established.

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The unique atomic resolution capability of field ion microscopy (FIM)[1] has not been taken advantage of in the past as a general thin-film characterization technique. Almost all of the early work has been on nucleation and early growth stages of metallic films by both FEM[2–4] (field emission microscopy) and FIM.[5–9] Some exploratory work with FIM of electrodeposits was done by Rendulic and Müeller.[10] Another relevant FIM study is that of Inal and Torma[11] who recently investigated electrodeposited black chrome. The present study reports for the first time the compositional analysis of thin films by the atom probe (AP) and the FIM structural imaging of both polycrystalline and amorphous semiconducting and insulating thin films.

With a growing interest in thin films for widely differing applications there is a definite need for fully characterizing them in order to establish structure-composition-property relationships. The complete characterization of surfaces and defects in thin solid films requires the detailed knowledge of the topography of the structure and chemical identity of its constituents. There are now a number of different characterization techniques available to give such information indirectly; however, each technique is heavily weighted for only one of the above two features. For the surface and depth profiling of thin-film coatings atom probe field ion microscopy (APFIM) has the distinct advantage of providing, quite directly, the structure as well as the composition.[12–14] The FIM portion shows the surface topography, including atomic details such as vacancies, interstitials, dislocations, and grain boundaries, while the AP portion of this instrument offers the chemical identification.

This letter is a preliminary report on novel experiments in imagining and analyzing sputtered thin-film coating of Ge, WO_3, Ni, Au, and Pt using a time-of-flight APFIM.

Films were deposited on molybdenum field ion tips by rf sputtering, using an MRC (Model 8502S) system with a gas-inlet system consisting of an MKS Baratron capacitance manometer, a Granville-Phillips closed-loop feedback controller and servo-controlled leak value, and a Ti-getter Ar purifier. The diffusion pump system was routinely pumped to 2×10^{-5} Pa before backfilling with Ar sputtering gas. The Mo tips were prepared by the usual electropolishing technique and no other surface treatments were given. Also the tips were not field evaporated in vacuum, so as to obtain an atomically smooth surface, prior to the film deposition. In the present work all the films were sputtered at 2.6-μm Ar pressure and at an rf power of 50 W. The substrate (tip)-target distance was kept constant between 50 and 55 mm. The deposition time was controlled to obtain estimated film thickness in the range 3000–5000 Å.

Details of the high-resolution TOF atom probe used in this experiment are given elsewhere.[15] This energy focused instrument, incorporating a 163° electrostatic energy analyzer, provides quite routinely a resolution $M/\Delta M > 1000$ measured at 10% peak level rather than 50% peak level. This allows for an adequate separtion between various masses $\frac{1}{3}$ or $\frac{1}{4}$ AMU (atomic mass unit) apart. A background pressure of 2×10^{-7} Pa is easily achieved after baking at 200–250 °C. The operating pressure of the image gases was $\sim6\times10^{-4}$ Pa, a pressure typical for a FIM with a channel plate image intensifier. The tip specimens were maintained at $\sim$85 K

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