Investigation of crystallinity of germanium thin films vacuum deposited on GaAs

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We investigated the crystalline quality of Ge thin films vacuum deposited on heated (1 0 0) GaAs substrates. Ge was evaporated using an electron beam and deposited to thicknesses of 100 and 500 nm, which were measured by a Dektak stylus-type instrument. These results were compared with the predictions of a cosine distribution law derived for the deposition system and found to be in relatively good agreement. The crystalline quality of the films was studied using scanning electron microscopy. Results have shown that epitaxy was strongly dependent on the substrate temperature, surface cleanliness and post-deposition annealing. Epitaxy was reproducibly achieved at a substrate temperature of \( T_s = 450 \, ^\circ\text{C} \). All films deposited at \( T_s = 350 \) or \( 400 \, ^\circ\text{C} \) were polycrystalline or amorphous, except one grown at \( T_s = 350 \, ^\circ\text{C} \), which proved to be monocrystalline. It is speculated that an anomalously clean and smooth substrate surface was responsible for this crystalline quality of films. In addition, it has been shown that post-deposition annealing of the films improved their crystallinity.

1. Introduction
The fabrication of reliable and reproducible ohmic contacts to GaAs has been a major obstacle in the development of semiconductor devices. The manufacturers of GaAs-based devices mostly use Au–Ge or Au–Ge–Ni alloy to form contacts. However, these contacts are difficult to reproduce reliably as they tend to deteriorate with age [1, 2]. In this work we attempted to deposit Ge epitaxially on semi-insulating (SI) Cr-doped GaAs using the electron beam vacuum evaporation system. As is known, a key parameter in depositing Ge epitaxially via vacuum evaporation is the substrate temperature \( (T_s) \). It has been found that optimum epitaxy occurs [3, 4] at \( T_s \) in the range 425–500 °C. However, the same Ge crystal can be grown at a temperature as low as 350 °C. Twinning is, however, observed [3] at lower temperatures. Motivated from these studies [4, 5], we thought it pertinent to investigate the effects of substrate temperature and subsequent high-temperature anneals on the crystallinity of vacuum deposited Ge. The samples thus prepared were analysed using a scanning electron microscopic (SEM) technique. The details of the experimental procedure and consequent results are presented and discussed below.

2. Experimental
The General Electric Co. provided highly polished (1 0 0) Cr-doped SI and Si-doped (about 0.001 Ω cm) GaAs substrates which needed no further polishing. Thus, only the Molecular Beam (MB) etch was used in preparing the substrates.

2.1. Evaporation procedure
After preparing the GaAs substrate, the evaporation chamber was readied. The substrate was then mounted on a graphite block and covered with the appropriate thin quartz plate substrate mask. The top plate was set in place on the top plate of the chamber and aligned so that the crystal monitor was between the substrate and Ge source. The alignment was precise and duplicated for such deposition so that the cosine law relating the crystal monitor reading to the actual film thickness was reliable. Before each deposition the substrate was etched to remove any residual oxide or carbon layer and the Ge source and graphite boat were outgassed. After this had been done, the liquid \( N_2 \) trap was refilled and the system was allowed to pump down to a low pressure. The substrate was then heated to the desired deposition temperature and allowed to stabilize. Once the proper deposition rate had been established of \( 0.37 \, \text{nm s}^{-1} \), the shutter was rotated out of the way while at the same time the digital frequency reading and the time were noted. The typical chamber pressure during the deposition was about \( 1.3 \times 10^{-4} \, \text{Pa} \).

Upon completion of the run, the sample was allowed to cool for at least 1 h in vacuum. After the cooling period the chamber was brought up to atmospheric pressure, the top plate was removed and the sample was removed from the holder. The orientations of the sample were noted with respect to the crystal monitor so that the thickness of the Ge layer could be calculated for various positions on the sample using a cosine distribution law.

2.2. Annealing procedure
Annealing of Ge films was conducted in a diffusion furnace. The samples were capped with approximately 90 nm Si₃N₄ (or SiO₂) to prevent out-diffusion of As,
Ga or Ge during heating. This was done using a Tegal r.f. deposition unit to sputter ammonia and silane at 400 °C for approximately 6 min. The coatings deposited on these samples had a bluish hue and a refractive index of 2.03 as measured by an ellipsometer, indicating that a reasonably good quality of Si₃N₄ films had been formed. Before each anneal the furnace was allowed to stabilize at the desired temperature for at least 12 h. The sample was then pushed into the flat zone of the furnace. 5 min were added to each anneal to allow the sample to reach the desired temperature. After completing the annealing, the sample was allowed to cool at the furnace entrance for 10 min, after which it was removed.

After the Si₃N₄ cap was etched away, it was rinsed thoroughly in H₂O and air-dried using the filtered air gun. The sample was cleaved into two parts of unequal size, and in all cases the smaller piece was etched with heated H₂O₂ to remove the Ge overlayer. The SEM was used to look at channelling on the Ge films left on the unetched samples in order to obtain information about the crystallinity of the annealed Ge layer.

2.3. Ge thin film analysis
All Ge films were grown at the same deposition rate of 0.37 nm s⁻¹ at a chamber pressure between 9.3 × 10⁻⁵ and 2 × 10⁻⁴ Pa as read on a Bayard Alpert-type ionization gauge. The substrate temperature was set at one of the three values 350, 400 or 450 °C, and films were deposited to nominal thicknesses of 100 or 500 nm.

Thicknesses were originally estimated using the cosine law of emission for a small plane source parallel to the substrate such that

\[ t = \frac{m \cos^2 \theta}{\pi \rho r^2} \]  

where \( m \) is the total mass deposited and \( \rho \) is the density (g cm⁻³). If \( t \) is the thickness of deposit just below the source at point 1, then its value is obtained from

\[ t_1 = t \left( \frac{r \cos \theta}{r_1 \cos \theta} \right)^2 \]  

\( \theta \) being the normal angle between the surface of the substrate and the direction of the vapour stream. The parameters \( r \) and \( r_1 \) are the distance from a small area at the source to the plane parallel surface of the substrate where the film is to be evaporated and to the point just below the source.

From the configuration of the system and the size of the mask used (13 mm × 13 mm), the ratios of the film thicknesses at various positions on the substrate to the measured thicknesses at the monitor were calculated to be

\[ \frac{t_2}{t_1} = 0.81 \quad \frac{t_3}{t_1} = 0.79 \quad \frac{t_4}{t_1} = 0.75 \]  

with \( t_2, t_3 \) and \( t_4 \) as the thicknesses at the near edge, middle and far edge of the substrate with respect to the source position. Thus, a film with thickness of 100 nm at the middle of the substrate would vary from about 103 to about 95 nm edge-to-edge according to the cosine distribution law.

Certain film thicknesses were determined by direct measurement using a Dektak stylus-type instrument. The step height for the film 2-1-89-1 (see Fig. 1) was measured on a 100 nm div⁻¹ scale and was found to show a change of 4.5 divisions as the stylus stepped up from the GaAs substrate to the Ge film. Thus, the thickness was approximately 450 nm.

The results of the Dektak measurements (see Figs 1 and 2 for raw data) are compared with the cosine law predictions in Table I. The Dektak measurements indicate that the cosine distribution law gives a reasonable estimate of the film thickness.

The crystalline quality of various films was analysed using SEM channelling. The films analysed in these ways were as-grown layers and samples that had been subjected were encapsulated in Si₃N₄, which involved heating them to about 400 °C for 6–10 min. In addition, samples were heated in the diffusion furnace to 658 °C for 24 h, 707 °C for 9 h, 753 °C for 3 h or 800 °C for 1 h.

The SEM channelling was used to study the crystalline quality of these films. Since the electron energy used in SEM was comparatively low (the beam energy...