In Situ Investigation of Band Bending during Formation of GaAs-Ge Heterostructures

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Symmetry-forbidden phonon Raman scattering is used to investigate *in situ* the formation of GaAs-Ge heterojunctions. Under epitaxial growth conditions the band bending in GaAs induced by the first monolayers of Ge decreases strongly for thicker overlayers. For amorphous overlayers the Fermi level remains pinned around midgap. A simple model is presented which explains the observed behavior. The development of the Ge phonons demonstrates crystalline growth for substrate temperatures $T_g \geq 300$ K and amorphous growth for $T_g = 100$ K.

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The GaAs-Ge system has received considerable attention for a long time, a fact which is caused primarily by the different nature of the band gaps of the two materials concomitant with a nearly perfect lattice matching.[1] The valence-band discontinuity ΔE_v is determined most reliably from photoemission experiments. Results of several groups have been summarized recently,[2] giving an average value of $\Delta E_v = 0.33$ eV. A second important feature is the potential variation across the interface. Mönch and co-workers performed detailed studies of these properties[3-5] using photoemission and work-function measurements. They find a Fermi-level pinning on UHV-cleaved GaAs (110) surfaces at around midgap for Ge coverages of less than one monolayer. They conclude that Fermi-level pinning is governed by chemisorption-induced defects (e.g., vacancies or antisite defects), as has been discussed for metal and oxygen overlayers before.[6] Attempts to trace the band-bending behavior of the interface to a Ge overlayer thickness larger than the electron escape depth of about 6 Å[5] seems questionable: Strong Ga and As core-level signals from atoms segregated near the free Ge surface prevent a probing of the interface.[5] In Fig. 1(a) we show the profile of valence- and conduction-band edges around the GaAs-Ge interface, as expected from a defect model. Both layers are assumed to be *n* type, with the Ge free surface being depleted naturally. The fixed valence-band discontinuity together with the Fermi-level pinning at the interface results in depletion regions on the GaAs as well as on the Ge side of the junction.

This is in contradiction to the recent work of Merlin *et al.*[7] who studied *n*-GaAs/*n*-Ge heterostructures grown by molecular-beam epitaxy. In their resonant inelastic light scattering experiments they have observed electronic excitations of a two-dimensional carrier system in the Ge layer. It is believed that the measured broad and asymmetric excitation line is due to intersubband transitions of electrons confined at the GaAs-Ge interface. Thus it seems possible to achieve interfaces with a negligible amount of interface states. A two-dimensional electron system is formed by the charge transfer from the donor states in GaAs to the conduction band in Ge. The resulting band scheme for such heterostructures is shown in Fig. 1(b).

In the present work we report on *in situ* investigations of band bending in GaAs during the formation of GaAs-Ge heterostructures. The barrier height has been measured from submonolayer coverages on clean UHV-cleaved GaAs (110) sur-

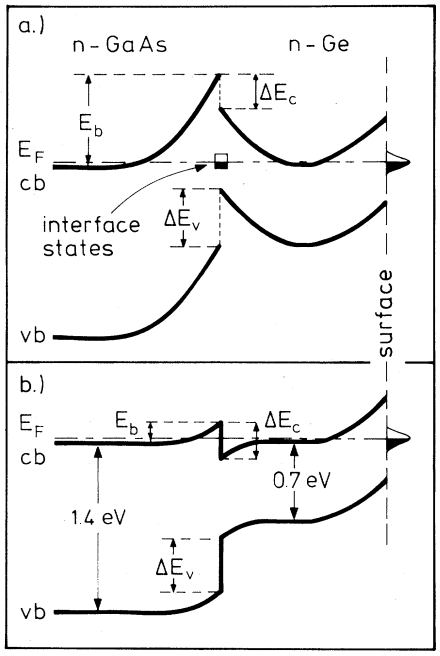

FIG. 1. Real-space energy diagram of a GaAs-Ge interface (schematically) (a) Fermi-level pinning at interface states and (b) potential variation in the absence of interface states.

faces up to Ge overlayers of about a hundred monolayers (~ 200 Å). The surface band bending in polar semiconductors can be determined from the Raman intensity of the resonantly excited symmetry-forbidden LO phonon, which depends strongly on the surface electric field.[8] This has been shown quantitatively by use of a Schottky-barrier arrangement on (110) surfaces of GaAs.[9] Raman scattering by LO phonons is not allowed in backscattering from those surfaces. Close to resonance, however, symmetry-breaking mechanisms are responsible for the observation of "forbidden" LO-phonon scattering.[9] Electric-field-induced scattering is dominant in most cases. It agrees qualitatively with a Franz-Keldish-type theory which gives, in the limit of weak electric fields E, an E^2 behavior for the LO-phonon intensity. As the barrier height E_b is also proportional to E^2 (Schottky model), the LO-phonon intensity reflects directly E_b, provided that the light penetration depth is smaller than the depletion width. The usefulness of this method in determining the Fermi-level pinning on clean and covered GaAs (110) surfaces has been demonstrated recently[10-12] and will be discussed for Ge on GaAs in the following.

The samples were prepared by cleaving single crystals of nominally 7×10^{17} cm^{-3} Te-doped GaAs bars in an UHV chamber with base pressure $<10^{-10}$ mbar. The sample temperature could be varied from 100 to 700 K. High-purity Ge was evaporated from an effusion cell. During evaporation with a maximum growth rate of 0.05 Å/s the pressure did not exceed 1×10^{-9} mbar. The film thickness has been controlled by a crystal quartz monitor. The Raman measurements were performed *in situ*. In order to fulfill the resonance condition for forbidden LO-phonon scattering and to keep the light penetration depth small we used the laser lines of a Kr^+-ion laser and a Stilben dye laser in the energy range around 3 eV, close to the E_1 gap of GaAs. The backscattered light [polarized (110)(110)] was collected and analyzed with a double-grating spectrometer and conventional pulse counting electronics.

Figure 2 shows three series of Raman spectra of TO and forbidden LO phonons in GaAs at various Ge coverages and different growth temperatures T_g. Each spectrum ranges from 30 to 40 meV. Ge thicknesses are given in monolayers (ML), where one ML corresponds to the distance of neighboring (110) planes, i.e., 2.0 Å. All spectra are normalized to the intensity of the TO-phonon mode, which does not depend on the surface electric field. The measuring temperature T_m was 300 K with the exception of the uppermost series, where $T_m = T_g = 100$ K, to avoid annealing effects.

In Fig. 3 the intensity ratio I_{LO}/I_{TO} for each series has been evaluated in terms of surface-

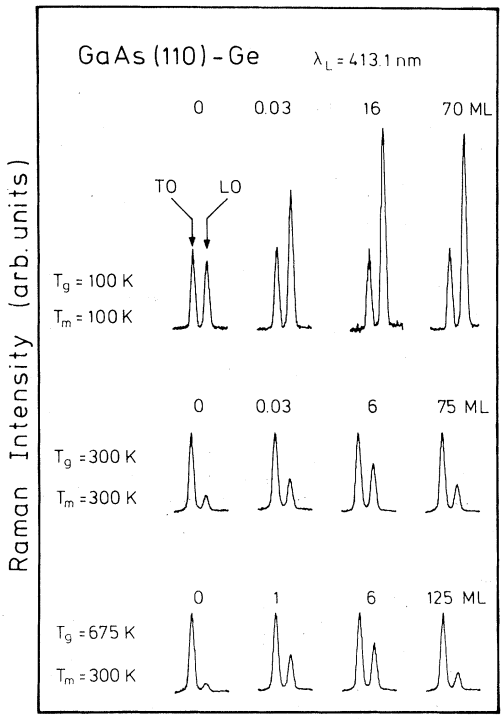

FIG. 2. Raman spectra of TO- and forbidden LO-phonon scattering in GaAs at various Ge coverages. T_g is the growth temperature, and T_m the sample temperature during the measurements.

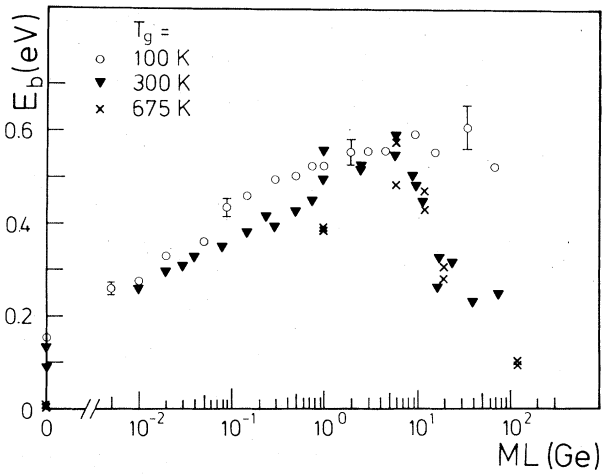

FIG. 3. Barrier height E_b as a function of Ge deposition.

barrier heights E_b: As I_{LO}/I_{TO} is in good approximation proportional to E_b,[9] the energy scale is fixed by two values. I_{LO}/I_{TO} corresponding to $E_b = 0$ eV (flat band) is determined from the freshly cleaved GaAs surface. To assure flat-band behavior, we measured the coupled phonon-plasmon modes close to the surface at low temperatures.[11] To get a second calibration point we attribute I_{LO}/I_{TO} of semitransparent metal Schottky barriers to the literature value $E_b \approx 0.65$ eV.[6] These samples have been prepared under the same conditions as the heterojunctions. As the absolute value of I_{LO} depends strongly on T_m (see Fig. 2), the scaling procedure has to be performed for each temperature separately. From this calibration we find the following for the GaAs band bending at the interface: The barrier height increases initially with Ge coverage for all growth temperatures investigated (100 K $\leq T_m \leq$ 675 K). For T_m = 100 K the band bending reaches a saturation value of ~ 0.6 eV at about 1 ML of Ge and remains constant within experimental error up to the thickest Ge layers grown. This is in contrast to the measurements at $T_m \geq 300$ K, where the barrier height drops drastically when the Ge coverage exceeds about 6 ML. The lowest measured value is $E_b \simeq 0.1$ eV for a 250-Å-thick Ge film deposited at $T_g = 675$ K.

We have also investigated the nature of the grown Ge films by analyzing Raman spectra obtained with $\hbar\omega_L = 2.41$ eV which is close to the $E_1 + \Delta_1$ resonance of Ge. Examples are shown in Fig. 4. Films grown at low temperature ($T_g = 100$ K) do not exhibit any sharp phonon structure. Their Raman spectra are typical for amorphous Ge[13] (top curve in Fig. 4). This spectrum has been obtained for a 140-Å-thick Ge film with use of a scattering configuration for which both first-order LO- and TO-phonon Raman scattering in GaAs are forbidden. Otherwise the weak structure of the amorphous film is dominated by the strong TO-phonon mode of GaAs at 33.4 meV. For Ge films grown at higher temperatures ($T_g \geq 300$ K) the optical-phonon line of crystalline Ge develops nicely. The first hints of the Ge phonons are observed already for films as thin as 3 to 4 ML. As shown in the lower part of Fig. 4 the intensity of the Ge phonon line increases strongly with film thickness, while the TO-phonon line of GaAs decreases as a result of absorption of light in the Ge film. Note the different energy scales used in Fig. 4. The phonon Raman spectra demonstrate directly that Ge films grown with a low evaporation rate at room temperature already

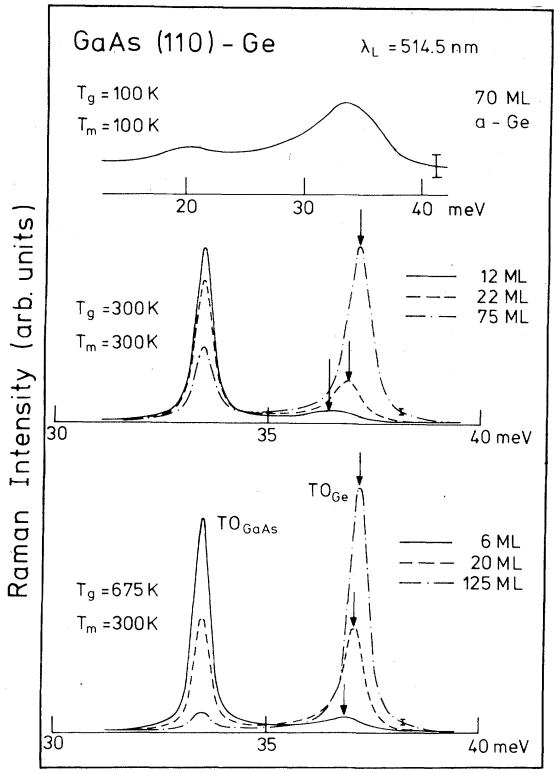

FIG. 4. Raman spectra of thin GaAs-Ge heterostructures grown at different temperatures. The arrows mark the phonon peaks of the thin crystalline Ge layers. Note the shift to smaller energies with decreasing film thickness which reflects the lattice dynamics of a thin Ge slab.

have a crystalline nature. Comparing the line shapes and intensities of the phonon modes with published data[13] shows, however, that room-temperature–grown films are polycrystalline with a grain size of the order of 10 μm. Overlayers of similar thickness grown at $T_g = 675$ K exhibit sharper, more symmetric and more intense phonon lines, indicating a much higher quality of the epitaxial films.

A simple model is proposed to explain our results. It does not involve any chemisorption-induced defects: The free, ideally cleaved GaAs (110) surface minimizes its energy by reconstruction. Dangling-bond energy states are swept out of the direct energy gap. Consequently, no band bending occurs.[14] Chemisorption of Ge atoms can lift the surface reconstruction, giving rise to dangling-bond states (both Ga and As unpaired bonds). The energy of these states is expected to lie within the band gap,[14] causing surface band bending. On the other hand, neither Ge-Ga nor Ge-As bonds create electron states inside the fundamental gap.[15,16] Thus, if we as-

sume perfect epitaxial Ge growth, all interface states will be removed after the deposition of one monolayer of Ge. E_F, however, is further pinned at probably slightly different energy at the free Ge surface. Consequently, for thin Ge films, there exists still considerable band bending at the interface. With increasing Ge thickness, E_b at the interface decreases resulting finally in a band scheme as shown in Fig. 1(b). For the amorphous films on the other hand there remain enough unpaired dangling-bond states to cause Fermi-level pinning at the GaAs side of the interface.

In conclusion, we have used resonant Raman scattering to investigate the interface barrier height between Ge and GaAs from the lowest coverages, where photoemission is believed to give reliable results, up to Ge overlayers of more than 250 Å thickness where real heterojunction life starts. We find strong evidence that the band bending in GaAs induced by low coverages of Ge is drastically reduced when epitaxial growth occurs. The idea that Fermi-level pinning on GaAs (110) is due to chemisorption-induced defects seems not to be generally applicable, because it is unlikely that such defects are annealed during epitaxial growth. This, however, would be necessary to explain the small interface barrier observed for thick epitaxial overlayers.

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