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C. M. Bertoni[(x)], C. Calandra[(x)], F. Mangini[(x)], S. Nannarone, F.Patella, P. Perfetti, C. Quaresima and A. Savoia:
MICROSCOPIC ASPECTS OF Si-Ge HETEROJUNCTION FORMATION.

ABSTRACT

We report evidence for the occurrence of a sharp transition in the electronic properties of heterojunctions formed by deposition of Germanium on Si(111) surfaces. Energy Loss Spectra have been taken for various Ge coverages and compared with theoretical calculations. The results indicate that the junction is abrupt and at low coverages Ge layers are deposited uniformly on the substrate. At 4-5 monolayers coverage modifications in the electronic structure appear caused by the onset of misfit dislocations.

The early stages of formation of heterojunctions have been object of recent investigations, where surface techniques were used to gain a better knowledge of the microscopical properties of the interfaces[(1-2)]. The work has been confined to materials with low lattice mismatch, as Ge-GaAs. In ref. (2) it has been suggested that interdiffusion of atomic species through the surface occurs in the Ge-GaAs system and it is crucially important in determining the electronic properties. On the other hand a comparison with the available theoretical results[(3-4)] can be made only if an abrupt heterojunction is formed.

In this letter we report new results concerning the electronic properties of heterojunctions formed by evaporative deposition of Germanium on cleaved (111) surfaces of Silicon. Our work gives evidence that the interface between these matarials is abrupt and shows the occurrence of a sharp transition on passing from low ($\theta<2$ monolayers) to high Ge coverages. Such a transition is imputed to the onset of misfit dislocations, which give rise to a high density of dangling bonds at the interface.

The absence of atomic interdiffusion is in agreement with the results on the mixing enthalpy of binary solid solutions of covalent semiconductors, showing that for high lattice mismatch between the end components the solution tends to segregate[(5-6)]. For the Ge-Si system, which has a 4% mismatch in the lattice constant, segregation is rather likely, so that abrupt heterojunctions are expected in a large range of temperature. The present study indicates also at what coverages misfit dislocations start to from i.e. it becomes energetically favorable for the system to produce dislocations at the interface rather than to grow the Ge layers in uniform

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sheets with the Si lattice constant. Because of its plastic properties Germanium is expected to have significant dislocations. The minimum number of dangling bonds resulting from them is about 6 x $10^{13}/cm^2$, high enough to give important modifications to the electronic structure.

We report here on Electron Energy Loss Spectroscopy (ELS) on the Ge/Si interface. ELS data were taken on an "in situ" cleaved n-type Si(111) single crystal at different Ge coverages obtained by thermal evaporation and ranging from a fraction of monolayer to ~10 monolayers. The evaporation rate was determined by calibrating the source with a piezoelectric film thickness monitor. The monolayer coverage ($\Theta = 1$) was defined as that due to 7.8 x 10^{14} atoms/cm^2, corresponding to 1.7 Å Ge thickness. A 100 eV primary electron beam impinging on the sample at 45° was used and the reflected electrons were energy analized using a double pass Cilindrical Mirror Analyzer. During the deposition the substrate was held at room temperature with a base pressure of 2 x 10^{-10} torr. Auger spectra, taken after each evaporation, did not show appreciable oxigen or carbon contamination.

Fig. 1 shows a set of selected ELS spectra referring to the clean Si(111) surface and to the Ge-covered

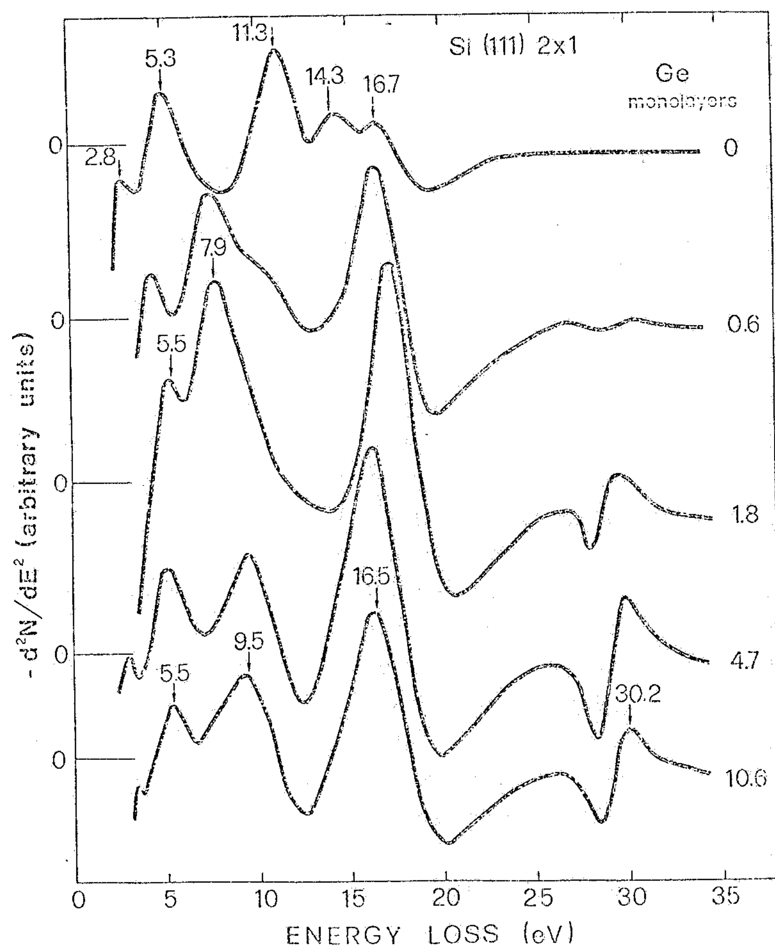

FIG. 1 - ELS spectra of Ge deposited on cleaved (111) Si for various overlayer thicknesses.

sample with different overlayer thicknesses (Θ=0.6, 1.8, 4.7, 10.6). All the features of the clean surface spectrum have been already identified[(7)]. In particular peaks at 16.7 and 11.3 eV correspond to bulk and surface plasmon respectively. The peak at 5.3 eV is a one-electron transition related to bulk Si band structure. The remaining losses at 2.8 and 14.3 eV involve mainly transitions between back bond and empty surface states.

The analysis of the other curves shows that two important effects occur with Ge deposition. First at low coverages (Θ < 2 monolayers) the clean surface features disappear and are replaced by a strong peak at 7.9 eV, the bulk Si plasmon is slightly shifted at higher energy (17.4 for 1.8 monolayers) and a new structure appears in the 4.7 - 5.2 range. At these coverages transitions from Ge d-core levels are also growing up.

The second important effect is the drastic change, which occurs for $\Theta \sim 4$ monolayers in the range of losses between 6 and 10 eV: the Ge induced peak at 7.9 eV is completely removed and a new structure at 9.5 eV appears with different shape. Further deposition of Ge does not modify the location of the main structures appreciably, the evolution of the spectrum being almost ended at 4 - 5 monolayers deposition. This final spectrum does not correspond to the one obtained for clean and annealed Ge (111) surfaces(8), although the structure at 5.5 eV, due to bulk interband transitions(9), and the plasma peak are still present. The main difference lies in the peak at 9.5 eV, which in the clean surface spectrum is replaced by a loss at 8.5 eV, attributed to surface transitions(8). The only possible explanation of this difference is that a significant number of defect induced states are present at the interface. This conclusion is borne out by the resemblance of our spectrum at high coverages with ELS data for Ar^+ sputtered surfaces, showing a similar peak at 9.9 eV(8) . Also the width and shape of the peak at 30 eV, which is kown to be sensitive to the surface roughness, are considerably different from the data for the clean surface. We interpret such defect induced transitions as the consequence of the onset of misfit dislocations at the interface.

As regards the nature of the losses at low coverages we first notice that the shift in the plasma energy and the structure at 4.7 - 5.2 are due to interface plasma modes. In the large wavevector limit the condition for the existence of these modes is given by $\varepsilon_{Si} = -\varepsilon_{Ge}$, where ε_i is the effective dielectric constant of each medium, having the form $\varepsilon_i = 1 + \omega_p^2/(\delta^2 - \omega^2)$(10). The roots of this equation give plasma modes at the energies $\omega_1 = 4.6$ eV and $\omega_2 = 17.1$ eV in good agreement with the observed losses.

To understand the features in the electronic structure which determine the peak at 7.6 eV, we performed tight binding calculations of the surface energy bands, assuming a monolayer coverage with Ge atoms placed on onefold or threefold positions. The surface was simulated by the well known slab scheme(11-12). The slab consisted of 16 layers of Si substrate and an ordered monolayer of Ge on each surface. Changes in the electronic configuration and charge transfer effects were handled as in ref. (12). Our calculated bands are given in Fig. 2 and 3. Although significant differences arise in the details, some important features of the electronic structure do not depend on the geometry. In particular we notice that in both cases the gap accomodates a couple of surface bands degenerate at $\bar{\Gamma}$ and only partially filled. They are originated from π Ge levels and are localized with considerable charge on the first layer. Also the largest gaps of the projected bulk band structure show Ge induced features. Among them the most pronounced is a s-derived band, crossing the wide gap between -4 and -6.4 eV. It is not well defined from half $\bar{T}$ and $\bar{\Sigma}$ directions to $\bar{\Gamma}$ because it mixes with bulk states.

The behavior of σ levels is more sensitive to the surface geometry. Calculations with the head-on configuration give a nearly flat band at -2 eV arising from bonding combinations of sp_z orbitals. For Ge on threefold sites the p_z levels are considerably spread out and localized states are found only near -2 eV. Back bond states of Si give rise to a double degenerate band at $\bar{\Gamma}$, which split along symmetry directions.

Antibonding combinations of sp_z orbitals are responsible of the empty bands along $\bar{T}$ and $\bar{T}'$ directions near the upper edge of the gap.

Based on these theoretical results the loss at 7.9 eV is identified as due to transitions between Ge induced s-bands near -6.0 eV and the π bands in the gap. Such transitions are possible for both geometries and are typical of low depositions. For thicker films in fact the π bands sink into the valence band and change their composition to resemble the back bond states of the free Ge surface(13). Empty π states can exit only at low coverages, where the electronic configuration of the Ge atoms is not yet descrided by the sp^3 hybridization characteristic of the covalent bond.

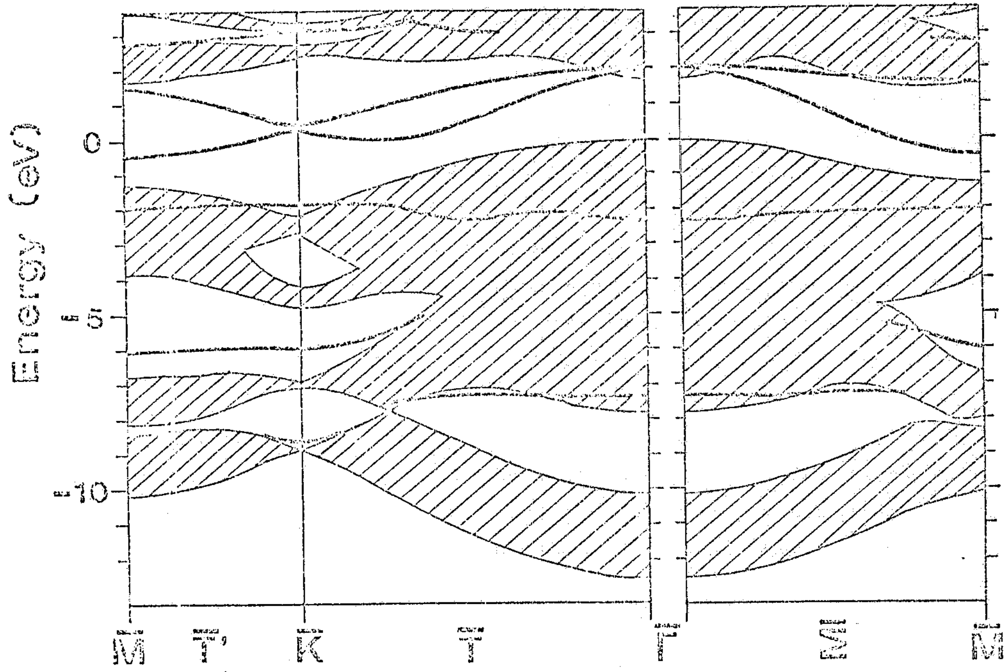

FIG. 2 - Surface band structure for Ge monolayer deposited on cleaved (111)Si in onefold position. The projection of bulk Si states onto the (111) surface is indicated by hatched areas.

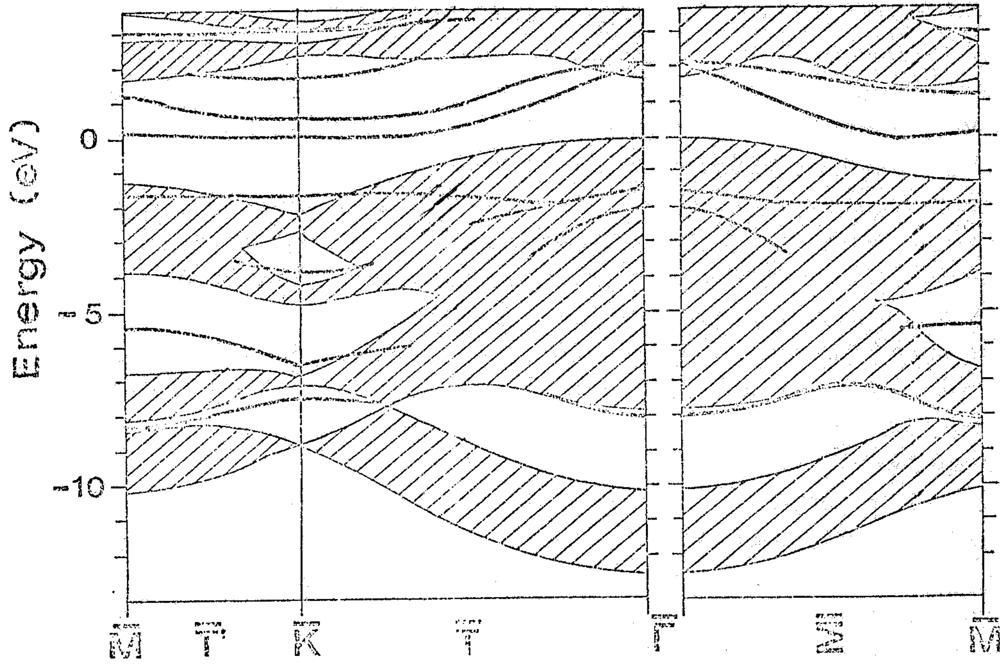

FIG. 3 - Surface band structure of Ge monolayer deposited on (111)Si in threefold position.

The agreement between our theoretical model and the experiments strongly indicates that the junction is abrupt and no interface diffusion takes place at room temperature.

Theoretical support for the identification of the 9.5 loss at high coverages comes from the results of tight binding calculations for 60° dislocations in Ge[14]. The theoretical density of states for atoms lying in the dilated region of the core of the dislocation shows an empty band of localized states near the conduction band bottom, built up with sp orbitals. Based on this result it seems possible to interpret the 9.6 eV excitation as due to transitions from low lying back bond states of Ge to this empty band.

REFERENCES

(1) P. Perfetti, D. Denley, K.A. Mills and D.A. Shirley; Appl. Phys. Letters 33, 667 (1978); D. Denley, K.A. Mills, P.Perfetti and D.A. Shirley; J. Vac. Sci. Technol. (in press).

(2) R.S. Bauer and J.C. Mc Menamin; J.Vac. Sci. Technol. 15, 1444 (1978).

(3) W.E. Pickett, S.G. Louie and M.L. Cohen; Phys. Rev. Letters 39, 109 (1977).

(4) G.A. Baraff, J.A. Appelbaum and D.R. Hamman; Phys. Rev. Letters 38, 237 (1977).

(5) M.B. Panish and M.Ilegems; Progress in Solid State Chemistry (Pergamon Press, 1972), vol. 7.

(6) V.T. Bublik, S.S. Gorelik, A.A. Zaitsev and A.Y. Polyakov; Phys. Stat. Sol. (b) 66, 427 (1974).

(7) H. Froitzheim; Topics in Current Physics (Springer, 1977), vol. 54.

(8) R. Ludeke and L.Esaki; Phys. Rev. Letters 11, 653 (1974).

(9) R. Ludeke and A. Koma; Phys. Rev. B13,739 (1976).

(10) L.J. Brillson; Phys. Rev. Letters 38, 245 (1977).

(11) C.K. Pandey and J. C. Phillips; Phys. Rev. B13, 750 (1976).

(12) C. Calandra, F. Manghi and C.M. Bertoni; J. Phys. C 10, 1911 (1977).

(13) S. Nannarone et al.; (to be published).

(14) R. Jones; Phil. Mag. 36, 677 (1977).