RELATION BETWEEN SURFACE CRYSTALLOGRAPHY AND SURFACE ELECTRONIC STRUCTURE OF A SUPERLATTICE.

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Profound gradual changes of surface state energies were predicted for varying surface terminations of the periodic crystal potential in onedimensional models [1]. This situation can be realized in superlattices with different thicknesses of topmost layers. For the ideally terminated (100) surface of a very thin superlattice $(GaAs)_2(AlAs)_2$ the shift of the energy of the surface state over the whole minigap in the lower part of the valence band has been found for different terminations of the topmost layer. In the center of the surface Brillouin zone the surface state shift follows model trends.The changes of the energy distribution of photoemitted electrons as determined from the one-step photoemission calculation [2] indicate that experimental observation by the surface sensitive technique of angular resolved photoemission should be feasible and preliminary data indicate this. The results show a straigthforward tuning of surface electron structure by geometrical means.

1 Introduction

Electronic surface states, i.e. states spatially localized at the crystal surface, can exist at energies corresponding to the band gaps of the infinite crystal. Their localization is given by the fact that electron propagation is impossible in both directions perpendicular to the surface: into the crystal bulk (band gap) as well as into the vacuum (surface potential barrier). The energy of the surface state within the band gap is determined by quantum mechanical matching of general solutions for the crystal and vacuum halfspace at the surface. In a simple one-dimensional nearly-free-electron model the energy of the surface state has been shown to be determined by the position of the termination of the periodic potential. For the sine-type potential the energy of the surface state has been shown to change from one edge of the band gap to another within approximately one half of the cut position period while in the other half no surface state has been found [1]. [1].

In simple crystals the choice of the periodic potential termination cannot be realized and the above analysis represents an academic model case only. In artificially grown superlattices where the translation symmetry is increased in one direction (e.g. in the crystal growth direction in the molecular beam epitaxy) and can be determined with a single atomic layer precision, however, the choice of the periodic potential termination becomes possible. Just by different termination of the growth within the superlattice period such samples can be prepared. In superlattices, the enhanced translation period is responsible for creation of new superlattice gaps (also called minigaps) where surface states can also exist.

The experimental confirmation of such shifts of the energy of the surface state has been performed for the Ag-Au(111)superlattice [2] by means of angle-resolved photoemission in the minigap situated close below the Fermi level. Superlattices with alternating 8 layers of Ag and 4 layers of Au with twelve different terminations (up to 8 Ag and up to 4 Au atomic layers) have been prepared by molecular beam epitaxy and analyzed in situ.

Compositional semiconductor superlattices are of considerable importance. Well-matched systems composed of layers of GaAs and AlAs have been investigated in detail, in particular their bulk electrical properties. Here, surface effects will be studied in these superlattices.

2 Theory

The photoemission current is calculated within the one-step model. The initial states are represented by a half-space Green function. The basis set consists of the 4s and 4p atomic orbitals of Ga and As and the 3s and 3p orbitals of Al. The associated Hamiltonian matrix is calculated according to the Extended-Huckel-Theory. The parameters for GaAs and AlAs are adjusted to give the correct

[1] A surface state energy dependence on the magnitude of the surface barrier has also been found there. Experimental observation of this change has been performed on "internal" surfaces of GaAs/AlGaAs superlattices [3, 4]

value of the valence band offset 0.45 eV between GaAs and AlAs. The final state in photoemission is a time reversed LEED-state determined by matching the solution of the complex band structure to the vacuum solution, representing the surface by a step potential. For more details see a recent paper [5] and references therein.

3 $(GaAs)_2(AlAs)_2$ Superlattice

The bulk of the "2x2" superlattice consisits of pairs of GaAs bilayers alternating with pairs of AlAs bilayers.The superlattice period in the direction perpendicular to the (100) surface is twice as long as that of its components and the corresponding Brillouin zone dimension becomes four times shorter (zinc-blende structure changes into tetragonal). The electronic structure of this superlattice has been studied in the past, both, theoretically [6] and experimentally [7]. The valence band can be approximated by folding the valence band of the bulk material (e.g. GaAs) into the smaller Brillouin zone corresponding to the increased translational period of the superlattice in the growth direction .
In addition, at the Brillouin zone edges, the superlattice band gaps open up. In particular, the lowest minigap (situated about 5.5 eV below the valence band top), predicted in theoretical calculations has been confirmed experimentally by means of the band mapping from the angle-resolved photoemission data. The upper half of the valence band is rather complicated due to the overlap of more branches of the band structure there (heavy and light hole branches intermixing with the split hole branch).
Here, the ideally terminated superlattice $(GaAs)_2(AlAs)_2$ with the unreconstructed 1x1 (100) surface will be investigated with the metallic atomic layer on the surface. For comparison of different terminations the models with two and one GaAs bilayers and two and one AlAs bilayers are treated.

4 Results

As we intend to analyze the normal photoemission spectra in detail, the relevant part of the electron band structure will be that along the line from the centre of the Brillouin zone Γ to its edge at Z (ΓZ=1/4 ΓX). The bulk band structure was shown and analyzed in our recent publication [5]: Fig.8 there shows the band folding into the smaller Brillouin zone as well as minigaps formed at its edge. The lowest one is the largest and extends approximately between -6 and -5 eV (the energy is related to the top of the valence band).
For the superlattice terminated by two GaAs bilayers a pronounced surface state has been found in the vicinity of the lower edge of the minigap. The density of electron states decomposed according to the layers and symmetry (Fig.1a) shows this state which decays uniformly from the surface and penetrates till the third bilayer. A more detailed analysis shows predominantly Ga s-character of this state and a rather smaller contribution of As orbitals (not shown here). The superlattice terminated with one GaAs bilayer has the surface state with energy around -5.3 eV (Fig.1b) and for that terminated by two AlAs bilayers the surface

state becomes a resonance at -4.8 eV (Fig.1c) with rather deep penetration into subsurface layers. Finally, for a termination with one AlAs bilayer no surface state or resonance is found in the vicinity of the lowest minigap (Fig.1d).
Thus, the surface state at $\bar{\Gamma}$ in the lowest minigap behaves in close analogy with a simple onedimensional model: also in this quasionedimensional situation the surface state energy shifts from one gap edge to another under terminations within one half of the superlattice period while the surface state is absent in the other superlattice half-period.
So far we discussed the surface state in the center of the surface Brillouin zone $\bar{\Gamma}$. Energy changes with different terminations of the superlattice for the whole surface state band $E(k_{||})$ are shown along several high symmetry lines of the surface Brillouin zone in upper parts of Fig.2. Projections of the electron bulk bands are represented by grey regions and surface and resonance bands are depicted by black lines there. For example, the surface band branch in the vicinity of the center of the surface Brillouin zone is influenced similarly: due to narrowing of the minigap along $\bar{\Gamma}\bar{J}$ and $\bar{\Gamma}\bar{J}'$ the corresponding energy shifts decrease in magnitude but relatively to the local gap their shifts are analogous to those at $\bar{\Gamma}$.
In the lower parts of Fig.2 the calculated normal photoemission spectra are shown for "2x2"superlattices with different terminations at the surface. The light is incident along the[110] direction and is polarised in a plane spanned by the [110] direction and the surface normal. The polar angle of incidence is 45^0. The energy of the exciting radiation in the range 20-38 eV is indicated next to individual curves. The clear nondispersive peak belonging to the superlattice surface state is visible at most excitation energies and moves to lower binding energies under different terminations in a close correspondence to the density of states profiles from Fig.1 with two GaAs bilayers till one AlAs bilayer in Figs.2a-d. The peak height and the magnitude of the energy shift imply that these effects should be observable in standard angle-resolved photoelectron spectroscopy.

5 Conclusions

The surface state shifts due to different terminations of the periodic potential at the surface discussed earlier in simple onedimensional models have been found also in a realistic situation: in semiconductor superlattices with very thin components of GaAs and AlAs. In the quasionedimensional case of the $(GaAs)_2(AlAs)_2(100)$ superlattice surface state shifts have been discovered for terminations with two or one bilayers of GaAs or Al As at the surface. Surface state shifts over the whole gap width and into the neighbouring band have been detected in the lowest minigap within the valence band.
Calculations, performed in the one-step model of photoemission,document these shifts, characterize the origin of the surface states and indicate that these effects should be observable in angle-resolved photoelectron spectroscopy.
The molecular beam epitaxy technique which enables to terminate the superlattice growth with one atomic layer precision provides a straightforward way of tuning their surface electron structure by geometrical means.

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FIGURE CAPTIONS

Fig. 1

Density of electron states for $(GaAs)_2(AlAs)_2$ (100) superlattice in the center of the surface Brillouin zone $\bar{\Gamma}$:the DOS is resolved by layers with the surface layer at the top (metal atomic planes only shown here) and by the orbital symmetry. The superlattice is terminated by: (a) two bilayers of GaAs, (b) one bilayer of GaAs, (c) two bilayers of AlAs and (d) one bilayer of AlAs at the surface.

Fig. 2

Surface electron structure (upper part) and normal photoemission spectra (lower part) of the $(GaAs)_2(AlAs)_2$ (100) superlattice. The gray regions denote projections of the bulk bands; dotted lines represent surface state and resonance bands. Superlattice terminations (a)-(d) are the same as in Fig.1.