ELECTRONIC STRUCTURE of ORDERED METAL OVERLAYERS on Si(111) SURFACES

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The electronic states of ordered Si(111) $\sqrt{3}x\sqrt{3}$:A1 and $\sqrt{3}x\sqrt{3}$:Ag and $\sqrt{19}x\sqrt{19}$:Ni structures have been studied over a range of metal coverages with core and angle-resolved valence band photoelectron spectroscopy. We report a new Si(111) $\sqrt{7}x\sqrt{7}$ A1 structure which arises at <0.5 monolayer coverage and surface related core level chemical shifts for these surfaces. Dangling bond derived bands are found for all the surfaces which for A1 and Ag have a dispersion of 0.4 eV. New structural models are proposed for all of these surfaces.

The interaction between silicon and metal overlayers has been the subject of many studies with LEED, EELS, Auger, and photoelectron spectroscopy. Most studies of the electronic structure have been made on disordered overlayers. In this paper we report on angle-resolved valence band photoemission and surface core level chemical shift measurements performed at the Stanford Synchrotron Radiation Laboratory. Ordered silicon-metal surfaces were studied where the number of metal surface atoms range from <0.1ML Ni to 0.5ML Al to 1.0ML Ag. Angle-resolved photoemission measurements used a new multi-detection spectrometer with an angular resolution of $\pm 1^{\circ}$ and an energy resolution of $1\%^{[1]}$ A differentially pumped ion gun was used for cleaning the Si-substrate and the surface cleanliness and ordering was checked with Auger and LEED. The Silicon-metal structures have been prepared by evaporating controlled amounts of metal onto a clean room temperature Si(111) 7x7 surface. This generally results in a metal covered surface that shows a 7x7 reconstruction, and does not necessarily correspond to an ordered metal overlayer. To obtain the ordered silicon-metal overlayers, the surfaces have to be annealed. Figure 1a shows for the surfaces studied the emission in the normal direction for $h_{\nu} = 22$ eV which was emphasized because the intensity from the dangling bond on the clean 2x1 surface has a local maximum. We discuss first Ni and then Al and Ag.

Comparing the photoemission from the clean 2x1 and 7x7 surfaces²¹ with the impurity stabilized $\sqrt{19} \times \sqrt{19}$ (R19) we can identify the dangling bond emission on all three surfaces. The dangling bond is a sharp feature and has a strong dispersion (0.6 eV) in some directions of k space for the 2x1 while for the 7x7 and R19 surfaces all the emission is broader. The emission reaches up to the Fermi level for the 7 x 7 surface, while this is not conclusive for the R19 surface. The emission from the Ni 3d-states gives an increase in the peak at -3 eV at this concentration while for disordered monolayer Ni-coverage the peak is at -2.4 eV. In our first studies, the Si(111) R19 was obtained as an unintentional impurity stabilized surface after long annealings at quite high temperatures (1000-1200°C). Auger always showed some Ni impurity. To establish the concentration of Ni atoms needed to get a good R19 structure, controlled amounts of Ni were evaporated from an electroplated tungsten filament and then annealed at 800°C. At this temperature the uncontrolled diffusion of impurity Ni to the surface was negligible. We find that excellent R19 LEED-patterns can be obtained with less than 0.10 ML of Ni.



This rules out the possibility that the surface reconstruction involves a monolayer of silicide. Rather, the unit cell of 19 Si-lattice sites contains only one Ni atom.

The similarity in the angle-resolved photoemission from the Si(111) 7x7 and R19:Ni surface suggests that the two reconstructions are quite similar. Also since the silicide, NiSi₂, is known to grow expitaxially on Si(111) at the annealing temperatures used, it is reasonable that the geometric configuration for the Ni atoms on the R19 surface involves bonding similar to the silicide structure. The model we propose in Fig. 2 is derived from the intrinsic 7x7 reconstruction model^[3] previously obtained. The energy minimization technique shows this 7x7model has energetically favorable ringlike structures of up and down atoms. We thus propose for the Ni R19 that the raised three atom "ring" is surrounded by 9 down atoms followed by 15 up atoms. The resulting up-down pattern shown in Fig. 2 has 10 up and 9 down atoms, close to the 50/50 ratio expected from the lowered atoms to the raised in the 2x1 and 7x7 reconstructions. In the R19 model, the Ni-atoms sit in the hollow position between the first two Si-layers, and with respect to the silicide, the atoms above and below are missing in the sixfold site. The Ni-Si distance for this position is very close to the value in the silicide because the lattice parameter of the silicide (5.406 A) is an excellent match to that of silicon (5.428 A). To make the geometry even more similar to the silicide configuration, the three Si atoms in the top layer should be raised and the three second layer atoms lowered.

Al and Ag behave differently than Ni and new surface structures arise at higher coverages indicative of ordered metal overlayers rather than an impurity stabilized Si structure. The polar and azimuthal angle-dependence of the photoemission from the overlayer surfaces are quite distinctive when all Si dangling bonds are saturated by metal adatoms. Particularly we have studied the new states that replace the dangling bond on the Al and Ag overlayer structures. In Fig. 1b we show examples where these states are strong and for reference we also show a 7x7 spectrum where the low energy (-2 eV) surface state is seen. The emission from this state on the clean surface has a three-fold symmetry, peaking towards the [112] direction. We interpret it as a backbond state, since it does not have the p_7 , S character of a dangling bond.

Fig. 2 Proposed model for the nickel impurity stabilized $\sqrt{19x}\sqrt{19}$ surface based upon the buckeled ring concept for the 7x7 surface: Note that this surface is a precursor of Ni silicide formation



For the aluminum overlayer surfaces we find a new state around -1.7 eV, i.e., intermediate in energy between the dangling bond and the back bond for the clean surface. This extrinsic state emission has a strong azimuthal and polar angle dependence. For p-polarized light with $\theta_j = 45$ degrees, we find the maximum intensity at 25 degrees polar angle with k parallel in the [112]-direction. The strong similarity with the emission pattern from back bond on clean Si(111) 7x7 indicates that the final state scattering is similar in the two cases. This is consistent with the aluminum atoms in the 3-fold hollow site, but <u>not</u> on the 3-fold site with a second layer silicon atom below. For the silver overlayer surfaces, an interface state at -1.4 eV arises that has a maximum emission at 25^o polar angle. The 3-fold azimuthal dependence is, however, opposite to that for the R3 Al surface, i.e., we find maximum intensity for k₁₁ in the [112] -direction. We conclude the bonding direction is opposite for the two overlayer structures. This differs from earlier models which proposed the center of the clusters of 3 Ag atoms would be on top of a second layer Si-atom.

In Fig. 3b we show the experimental dispersion for the extrinsic state on the R3 Al surface. The directions probed in the experiment are indicated in Fig. 3a in an extended zone scheme showing both the R3 and the 1x1 surface Brillouin zones. We find a dispersion that is symmetric around a minimum at M' in the r'K'M'K' -direction. The absolute minimum of the dispersion is at the outer Γ ' point in the Γ 'M' Γ ' -direction. It is interesting to note that the shape of the dispersion with respect to the 1 x 1 surface Brillouin zone is the same as has been calculated for the hypothetical dangling bond band of the clean 1x1 surface.We propose that the extrinsic state on the Si(111) R3 A1 surface has enough character of the dangling bond so that the similarity in dispersion is not accidental. The effect of the Al overlayer is two-fold. First it makes the surface unit cell three times larger than for the 1x1 surface, which means that the dangling bond band will correspond to three bands in the surface R3 Brillouin zone. Secondly the Al-atoms bring one 3p electron per unit cell that is close enough in energy to interact with the dangling bond electrons. We thus end up with 4 electrons per unit cell, that can fill two of the three dangling bond derived bands. The experiment shows that there are two occupied bands, since the measured dispersion gives different energy values for states at two different M' points, which are equivalent points in the R3 surface Brillouin zone. Since the width of the peak is relatively large (FWHM = 0.7 eV) compared to the dispersion 0.3 eV, we have not been able to resolve the two bands in any spectra.

Our results show that the aluminum atoms contribute electrons to the extrinsic surface state since we find an increased intensity with increasing Al-coverage. As shown in Fig. 3, we find

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no difference in the dispersion of the surface state if the surface is a pure $\sqrt{7x}\sqrt{7}$ phase. Based on this similarity in electronic structure with the R3 phase, as well as the determined value of 0.5 ML Al coverage for the R7 surface, a model for the R7 structure is proposed elsewhere. Both the R3 and R7 models satisfy the criterion that there is an even number of electrons per unit cell that can contribute to the high energy surface state, i.e., counting the dangling bond electrons on Si plus the 3p electrons on the Al-atoms. The energy dispersion of the extrinsic surface state on the Si(111) R3 Ag surface is also shown in Fig. 3. The general shape is similar to the Al covered surface and is at 0.3 eV higher energy. There is indication of splitting into two peaks in spectra probing the outer Γ ' -point. From theoretical arguments, we suggest that the occupied surface state bands exist for the ordered Ag overlayer due to the extra electron compared to Al. There are 6 electrons in the surface unit cell of the R3 Ag surface (three 5s electrons on the Ag-atoms plus three dangling bond electrons on the Si-atoms) that are close in energy to interact and form three occupied bands.

In contrast to the emission from the R3 Al surface, the extrinsic surface state on the R3 Ag surface can also be seen in normal emission. We expect the highest energy peak of the dangling bond derived surface state to be seen close to the normal like most theoretical calculations show. The differences regarding the normal emission between the R3 Al surfaces would then be due to the difference in the energy position and thus occupation of the third extrinsic surface state band. This is reasonable for the commonly proposed model for the R3 with Al atoms in a 3-fold site since all dangling bonds will be changed by the bonding to the Aluminum. The same agreement holds for the R7 model that we are proposing in this paper.

The analysis of the core level shifts has show differences between the 2x1 and the 7x7 surface. Here we conclude by discussing analysis of the Al 2p on Si(111). At submonolayer coverages, a binding energy typically 0.15 eV higher than the metallic case is obtained. When the surface reconstructs to either the R3 or the R7, the binding energy further increases to 0.35 eV in both cases. The lineshape broadens with respect to the metallic case due to the Si-Al bond by 15%.

Fig 3 a. Directions probed in the $\sqrt{3}x\sqrt{3}$ surface Brillouin Zone. b. dispersion for the extrinsic state on the Al and Ag $\sqrt{3}x\sqrt{3}$ surfaces.

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References:

1)G.V. Hansson, B. Goldberg and R.Z. Bachrach, Rev. Sci. Instr., to be published.

2) G.V. Hansson, R.Z. Bachrach, R.S. Bauer, et al.: Surface Science, 99, (1980).

3) D.J. Chadi et al.: Phys Rev Lett, 44, 799, (1980).

