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Surface core-level shifts of Si(111)7x7

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Abstract: We show that a consistent analysis of the Si 2p core-level spectra from the clean Si(111)7x7 surface measured with synchrotron radiation requires more surface shifted components than used until now. We discuss this new decomposition scheme in relation to the structural model of this heavily reconstructed surface.

1. INTRODUCTION

The Si(111)7x7 surface is surely the most amazing reconstruction in surface science. Its complex atomic structure was elucidated by Takayanagi et al. in 1985 [1]. Their so-called DAS model is now widely accepted; it involves several special features e.g. dimers, adatoms, restatoms, a corner vacancy and a stacking fault in half of the unit cell (see Fig. 1).

Synchrotron radiation (SR) core-level photoelectron spectroscopy has now developed into a very powerful surface characterization method [2] linking structural and electronic properties. The information extracted from the Si 2p core level analysis relies on a decomposition of the spectra using curve fitting routines. Until now only three spin-orbit split doublets, that is two surface shifted components (S1 and S2) in addition to the bulk one B, have been used in this decomposition for the 7x7 surfaces (Fig. 2a). The assignment of S2, appearing as a small bump at lower binding energy (BE) as compared to the bulk line, either to the adatoms or to the restatoms is still a matter of controversy [3, 4]. S1 has no clear assignment at all, being eventually considered as resulting from the adatoms plus the atoms underneath binding to them [3]. The present situation is thus quite unsatisfactory especially in view of the fact that several contributions could be expected, when looking at the different constitutive entities of this heavily reconstructed surface. Using the high resolution beam lines now available at several SR facilities these surface contributions should be hopefully identified.

In this paper we demonstrate that the standard deconvolution scheme with only two surface shifted components is no longer acceptable and has to be revised. As a matter of fact we show that a consistent analysis reveals at least five surface contributions S*1 to S*5.

2. Si 2p CORE-LEVEL ANALYSIS

The way the decomposition of core-level spectra is performed is of crucial importance since it involves several assumptions and a number of adjustable parameters in the curve-fitting procedure. These parameters are the spin-orbit splitting (S.O.), the Lorentzian full width at half maximum (FWHM) representing the inverse core-hole lifetime (L), the Gaussian FWHM for the bulk (G_B) and surface (G_S) components representing both instrumental broadening and a material contribution (like phonons, inhomogeneities etc...), their branching ratio and the type of background used.

Indeed looking at the complexity of the 7x7 reconstruction, one could expect more surface shifted components than just S1 and S2 assumed in the standard decomposition scheme (see Fig. 2a). In this respect, it is worth mentioning that for the corresponding Ge(111)-c(2x8) reconstruction of germanium (much simpler than the Si(111)-7x7 one since it involves only two entities : the adatoms and the restatoms [5]), three surface shifted components have been identified (see Fig. 3a).

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Fig.1. DAS model of Takayanagi et al. [1]. (a) Top view. Atoms in (111) layers at increasing depths are indicated by circles of decreasing sizes. Adatoms are shown by large filled circles, rest atoms are shown with circles marked A and B to indicate rest atoms in the faulted and unfaulted halves of the 7x7 unit cell, respectively. (b) Side view a cut along the long diagonal of the 7x7 unit cell. Atoms that are behind this cut are shown with smaller circles than those along the diagonal. (Adapted from Fig. 1 of ref [3].)

Fig.2. The same Si2p core-level spectra acquired from the Si(111)7x7 surface at 150 eV photon energy (from Fig.1 of ref. [4]). The top one (a) is fitted with three spin-orbit split doublet components labelled B, S1 and S2 following the decomposition of Carlisle et al. [4]. The middle one (b) is also fitted similarly with three components B', S'1 and S'2 but the Lorentzian FWHM have been reduced to 35 meV, accordingly the Gaussians have been enlarged. The bottom one (c) is fitted with 6 components B*, S*1 to S*5. The fitting parameters are displayed in table 1.

Fig. 3. Ge 3d core-level spectrum from the clean Ge(111)-c(2x8) surface recorded at 110 eV analysed with 4 spin-orbit doublets by Göthelid et al. [5].

Fig. 4. Decomposition of the Si 2p photoelectron spectrum from the Si(100)2x1 surface with 5 spin-orbit doublets following the analysis of Landemark et al. [8], but with a Lorentzian width of 35 meV.

With this in mind, we have nevertheless synthesized many spectra obtained at different photon energies first with only these two surface components. Due to space limitation here, we just display in our Fig. 2a a spectrum acquired at $h\nu = 150$ eV in a very surface sensitive mode. The fitting parameters are given in table 1. Good fits are obtained using essentially the same basic parameters as used traditionally by Chiang's group [6]. To obtain this good quality we had (as they had) first of all to take a large value of the Lorentzian FWHM : ~ 0.15 eV. This is however unacceptable since it has been proved recently that for the Si 2p core-level L is ~ 0.035 eV (or even may be less) [7].

Second, we had (again as usually done [4]) to markedly enlarge the Gaussian widths - i.e. to 0.19 eV ($h\nu = 108$ eV) and 0.36 eV ($h\nu = 150$ eV) for the bulk and 0.23 ($h\nu = 108$ eV), 0.38 eV ($h\nu = 150$ eV) for the surface components - as compared to the instrumental resolution (in the range 0.16-0.22 eV). This is also unrealistic since comparison with the work of Landemark et al. [7] for the clean Si(100)-2x1 surface shows that, with a total energy resolution better than 70 meV and extremely well-resolved Si 2p spectra, 4 surface components (in addition to the bulk one B) are needed in the decomposition. In a very surface sensitive mode ($h\nu = 130$ eV), the Gaussian FWHM are respectively 250 meV for the surface components and 215 meV for the bulk one, using still a too large Lorentzian width (85 meV), which translates for the convolution process and practically equal χ^2 's into Gaussian FWHM of respectively 280 and 250 meV when using the correct inverse lifetime of the core-hole, that is 35 meV (see Fig. 3b).

Table I. Fitting parameters (using an integrating background) for the Si 2p spectra shown in Fig.2 and 4. All energies are in eV. The Lorentzian and Gaussian widths refer to the FWHM. Binding energy shifts are referenced to the bulk components. The figures of merit of the synthesis, the chi squared, are given for direct comparison, the spectra being normalized to the same number of counts: 100.

	Si(111)7x7			Si(100)2x1
	3 comp.	3 comp.	6 comp.	4 comp.
Spin-orbit splitting	0.608	0.608	0.608	0.602
Branching ratio	2.0	2.08	2.0	2.25
Lorentzian width L	0.15	0.035	0.035	0.035
Gaussian width G _B	0.36	0.45	0.31	0.25
Gaussian width G _S	0.38	0.50	0.35	0.28
χ^2	0.56	0.516	0.455	0.45
Surface shifts	S1: +0.33 S2: -0.76	S'1: +0.38 S'2: -0.72	S*1 -0.49 S*2 -0.21 S*3 +0.14 S*4 +0.46 S*5 +0.76	see [8]

With this last value, it is impossible to achieve good curve synthesis of the spectra from the 7x7 surface without accordingly enlarging furthermore the Gaussian widths (i.e. to 310 meV (S1, S2) and 260 meV (B) at 108 eV and to 400 meV and 440 meV respectively at 150 eV) as shown in Fig. 2b). We believe that such a huge broadening is unphysical, especially in view of the perfectness of this surface, and just indicates the need for additional components as one can readily expect in view of the comparative studies for the Ge(111)-c(2x8) and Si(100)2x1 surfaces where more components are necessary, even though the reconstructions are simpler than the Si(111)7x7 one.

The minimum number of components which we think has to be involved in the fit is 6 (B+S*1 to S*5); the corresponding decomposition and fitting parameters are shown in Fig. 2c and table 1. In view of the number of special entities present in the 7x7 reconstruction, this number is probably not exaggerated, even it might be underestimated since the Gaussian widths are still markedly larger at 150 eV than at 108 eV, as compared to the loss of instrumental resolution (about 25 meV). Presently we cannot attribute a given atomic assignment to each of them. Nevertheless, it is now clear that the decomposition of the Si 2p spectra with only two surface doublets is rather arbitrary and because of the unphysically large widths of the components surely incorrect; in particular, the S2 component has to be replaced by two new ones (S*4 and S*5) with the consequence that S2 by itself has no physical significance.

3. CONCLUSION

To conclude, we want to emphasize that the correct decomposition of the Si 2p core-level spectra from the 7x7 surface requires at least five other components in addition to the bulk one. Much work is needed with the highest resolutions available now and especially at low temperatures to extract the phonon broadening contribution to the Gaussian widths, before considering that the question of the Si 2p core-level decomposition from the quite complex Si(111)7x7 reconstruction is definitively solved[9].

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- [9] Note added in proof: having obtained after this symposium extremely well resolved new data at low temperature we can confirm the presence of several components, as we predicted, just by visual inspection of the spectra (Le Lay et al. *Phys. Rev. B*, to be published).