Chemisorption Bonding of $c(2 \times 2)$ Chalcogen Overlayers on Ni(001)

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Calculated low-energy electron diffraction spectra for $c(2\times2)$ overlayer structures of O, S, Se, and Te on Ni(001) show very good agreement with experiment for fourfold coordinated bonding sites and displacements of 0.90, 1.30, 1.45, and 1.90 ± 0.1 Å, respectively, from the center of the first layer of nickel atoms. These adsorbate-atom locations correspond to Ni-chalcogen bond lengths smaller than occur in bulk compounds, but comparable to those found in divalent Ni-chelate complexes.

It has been anticipated and hoped that reliable surface-structure analysis for chemisorbed overlayers might be attainable by analysis of low-energy electron diffraction (LEED) spectra. However, in recent work[1-4] the differences between theory and experiment leave some reservations regarding the general usefulness or reliability of this technique for the structural analysis of overlayer systems. Only in one case[2] has reasonably good agreement been achieved for several diffraction beams over a wide energy range, thereby permitting a reliable structural analysis. We wish to report (1) the ability of current LEED theory to provide detailed agreement with experiment which is as good as we have found previously[5] for the clean surfaces of nickel; (2) the application of LEED theory to determine the structure of $c(2\times2)$ chalcogen overlayers on Ni(001), a family in which the adsorbate size and electronic nature change in a systematic manner; and (3) Ni-chalcogen bond lengths for these chemisorbed structures which are smaller than corresponding bond lengths for typical bulk compounds or than suggested in previous work,[4] but comparable to divalent Ni-chelate bond lengths.

From our work we find that the single most important quantity required to achieve good agreement between theory and reliable experiment for *both* fractional and integral order diffracted beams is the adsorbate location. Variations in these structural parameters (~ 0.1 Å) cause marked changes in the spectra. We find that, after having established good agreement between experimental peak positions above ~40 eV, reasonable modifications in the adsorbate scattering potential, effective Debye temperatures, or electron damping (imaginary part of the electron self-energy) would improve line shapes and relative intensities of high- and low-energy peaks, but would not significantly change the structural parameters. As has been found for clean surfaces,[6,7] the uncertainties in the electron-solid force law for the adsorbate strongly affect calculated spectra in the low-energy region below ~ 40 eV where the details of the valence-electron distribution are more important. In particular, the intensity effects arising from the scattering in the transition region between vacuum and solid occur predominantly in this energy region.[8] We conclude that the good agreement between theory and experiment achieved in this work should be generally possible above ~ 40 eV with current LEED

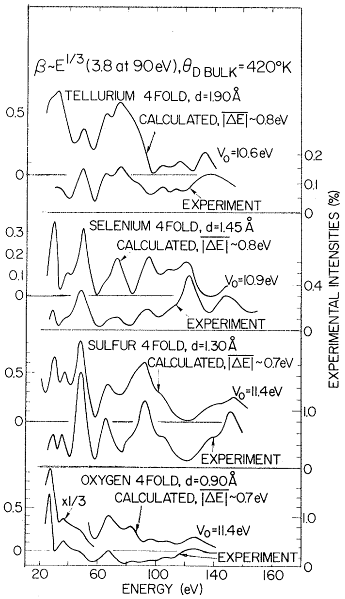

FIG. 1. Calculated and experimental (Ref. 9) $(\frac{1}{2}\frac{1}{2})$ beam spectra for the $c(2\times2)$ structures of the chalcogens adsorbed on Ni(001). For each chalcogen the fourfold coordinated bonding site (above the hollows between four nickel atoms) provides the best agreement with experiment for the noted displacements d (above the center of the first layer of nickel atoms). Similar good agreement between theoretical and experimental peak positions and line shapes for the (01) and (00) beams is also obtained (Ref. 11).

theory, despite its approximations, and hence should yield a reliable structural analysis of chemisorbed overlayers.

Figure 1 illustrates the close agreement we have achieved between the experimental results of Demuth and Rhodin[9] and theoretical calculations for the $(\frac{1}{2}\frac{1}{2})$ beam based on the layer–Korringa-Kohn-Rostoker (KKR) method.[10] In this method a total of 28 and 56 beams in the representation of Ni and adsorbate wave functions, respectively, were included. The calculations used eight phase shifts derived from the Wakoh potential for Ni and from a superposition potential for the adsorbate constructed by overlapping atomic charge densities. The atomic charge densities of Se and Te in a bcc lattice were superposed with a lattice constant equal to the interatomic spacing in the overlayer, while for O and S this lattice was contracted by ~30% to account for the additional background charge of the substrate. This method for obtaining the adsorbate scattering potential was readily available from well-tested bulk band-structure procedures. The inner potentials used for the calculations are indicated in Fig. 1, and were obtained by adding the change in work function experimentally observed[9] to the inner potential determined previously for the clean surfaces of nickel.[5] The electron damping (imaginary part of the potential) was also set equal to that found for the clean surface, while a bulk Debye temperature of 420°K and surface Debye temperatures of 295°K for Te and 335°K for O, S, and Se were used. The ±0.1-Å uncertainty in adsorbate displacement arises chiefly from the uncertainty in the experimental energy scale[9] and the variation of the inner potential (the real part of the electron self-energy) with energy which we have previously noted for the clean surfaces of nickel.[5] For a quantitative indication of the agreement between theory and experiment for the $(\frac{1}{2}\frac{1}{2})$ beams, each comparison made in Fig. 1 also contains the average value of the magnitude of the displacement between calculated and measured peak positions $\langle|\Delta E|\rangle$ for these optimal structures. The $\langle|\Delta E|\rangle$ values of $\lesssim 0.8$ eV for the $(\frac{1}{2}\frac{1}{2})$ beams are *also* found for the (01) and (00)

TABLE I. Determined chemisorption bond lengths and reported bond lengths of bulk compounds and Ni complexes.

	Determined distances (in angstroms)		Reported Ni-*X* lengths (in angstroms) Bulk compounds				Complexes
	d	Ni-*X* bond length	Ni_3X_2	$\mathrm{Ni}X$	Ni_3X_4	$\mathrm{Ni}X_2$	$[\mathrm{Ni}\text{-}X_4]$ [a]
O	0.90 ± 0.1	1.97 ± 0.05	···	2.08 [b,c]	···	···	1.84(4) [g] 2.03, 2.06 [h]
S	1.30 ± 0.1	2.18 ± 0.06	2.28 [c,d]	2.38 [c]	···	2.34 [c] 2.42 [e]	2.19–2.23(4) [g] 2.10–2.15(5) [g] 2.17(6) [g]
Se	1.45 ± 0.1	2.27 ± 0.06	2.36 [d]	2.50 [c,d]	2.47 [c,d]	2.53 [d] 2.49 [e]	2.32(4) [g]
Te	1.90 ± 0.1	2.58 ± 0.08	···	2.64 [c,f]	···	2.58 [d] 2.59 [f]	···

[a] All complexes are bichelate Ni II complexes where parentheses indicate the number of members in the chelate ring except for 2.03, 2.06 for oxygen complexes which are Ni II carboxylates.

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beams with similar good agreement between line shapes above 40 eV. The agreement obtained for each of these adsorbates in fourfold coordinated bonding sites is similar to that obtained for clean nickel surfaces[5] and is discussed and illustrated for these other beams in more detail elsewhere.[11] The good agreement between theoretical and experimental peak positions and line shapes of ($\frac{1}{2}\frac{1}{2}$), (01), and (00) beams for each adsorbate displacement d adds to our confidence in our determined structures.

In Table I we summarize the adsorbate displacements above the substrate, corresponding Ni-chalcogen bond lengths, and Ni-chalcogen bond lengths from other sources. Our determined bond lengths for O, S, and Se are slightly less than typical bond lengths found in bulk solids and are comparable to those of Ni-chelate complexes. However, the tellurium-Ni bond length is comparable to bulk bond lengths.

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Reversible Switching in Thin Amorphous Chalcogenide Films—Electronic Effects

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Experimental results suggest that (1) switching in thin chalcogenide glass films is fundamentally electronic, and (2) the regime of pure electronic initiation has been exposed.

We have investigated three aspects of switching in thin amorphous chalcogenide films[1]: (1) the response of unannealed virgin and "formed"[2] films to voltage pulses 2 nsec in duration, where heating is negligible; (2) the virgin threshold voltage as a function of pulse duration; (3) the phenomenon of "minor" switching.[3] The results indicate that (i) a critical electric field E_c must be reached in part of the film in order for conventional "delay-time" t_d switching to occur, and (ii) t_d has a shortest value t_s, the characteristic time required by the as yet unspecified electronic mechanism that produces switching.[1,4] The experimental results support the view that switching is fundamentally electronic,[1,4,5] and help elucidate the role of thermal effects under conditions where they can initiate the switching process.[6,7]

Samples were prepared in the following configurations: (a) $As_{49}Te_{51}$ glass prepared from 99.999%-pure elements was evaporated by electron beam onto a polished Al plate coated with 0.1 μm of Mo. These films were all of thickness l near 2 μm.[8] A spherical-tip graphite counterelectrode was set and maintained under slight pressure here and for samples in (b) below. "Off"-state resistances R_0 were typically between 10 and 50 kΩ.

(b) AsTe, As_2Te_3, and a few compositions in the Te-As-Si-Ge system were sputtered onto polished plates of Mo-coated Al in thicknesses of 0.5, 1.0, and 2.0 μm.[9] Here the R_0's ranged from