Determinants of Surface Atomic Geometry: The CuCl(110) Test Case

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The atomic geometry of the CuCl(110)-(1 × 1) surface is determined by dynamical analysis of low-energy electron-diffraction intensities. This surface undergoes a relaxation characterized by a ~30° Cu-Cl surface bond rotation, a 0.15 Å contraction of the top-to-second layer distance, and a 0.4 Å horizontal displacement of Cl relative to Cu. The relaxation is consistent with the "universal" structure deduced from the analysis of cleavage surfaces of tetrahedrally coordinated III-V and II-VI compounds, thereby revealing that this feature of the structure does not depend significantly on the ionicity of the compound.

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For decades the study of the dependence of surface atomic geometries on parameters characteristic of the bulk chemical bonding [1,2] (e.g., crystal class, lattice parameters, bonding character) has been a major topic in surface science. Historically, the cleavage faces of tetrahedrally coordinated compound semiconductors have been a fertile ground for the proposition and testing of such structure-bonding relationships because of their reproducible surface composition and extensive structure studies [3–5]. In recent years, however, the validity of earlier experimentally established scaling rules [6] has been questioned by a series of model predictions of the surface structures of the cleavage faces of zinc-blende-structure compounds [7]. The case of CuCl(110) emerged from these predictions as a crucial test case in which the scaling rules failed completely [7]. Our purpose in this paper is to report a structure analysis of CuCl(110) revealing that it is compatible with the experimentally established scaling rules and hence constitutes a critical piece of experimental evidence that atomic size and surface topology rather than bonding ionicity are the dominant determinants of the surface atomic geometries of the (110) cleavage surfaces of zinc-blende-structure compound semiconductors.

Zinc-blende (110) surfaces experience significant (~1 Å) relaxation of surface atomic positions from their bulk positions. Because of the reproducible 1:1 stoichiometry of these surfaces, the questions of the dominant driving force of the relaxations and their correlation with bulk structural and energetic parameters may be posed precisely. The earliest quantitative relaxation model predicted a link between relaxation and ionicity based on the small-molecule chemistry of the threefold-coordinated surface species [8]. According to this model, the surface anion and cation of mostly covalent III-V compounds would assume pyramidal p-like and planar sp^2-like bonding configurations, leading to the observed bond rotation, whereas their counterparts on the more ionic II-VI compounds would not. Yet, all geometries subsequently determined appeared to be largely independent of the ionicity of the compound, exhibiting an approximately constant bond rotation angle of $29° \pm 3°$ [4,5]. Moreover, atomic displacements were found to scale in such a way that all materials exhibit the same basic structure when dimensions are normalized to the bulk lattice constant [6]. The current interpretation of these results is that the topology, or atomic connectivity, of the cleavage surfaces is the dominant factor which defines surface atomic relaxations [5]. For (110) surfaces, this topology is compatible with an *activationless* bond-length-conserving surface bond rotation. The driving force behind this relaxation is the lowering of the surface electronic energy via rehybridization of the surface and backbonds [9].

These results and interpretation have been challenged by recent theoretical calculations which revive the notion of dependence of the relaxation on ionicity [7]. They predict a decline of the bond rotation angle of the (110) surface with increasing ionicity, due to the Coulomb interaction between the top anion and the second-layer cation. At the upper limit of ionicity scale in the family of zinc-blende compounds (e.g., the I-VII cuprous halides), the calculations indicate that the (110) surface should be unrelaxed.

The present structure determination on (110) cuprous chloride (CuCl), the first performed on a I-VII compound, provides a critical test of this prediction and of the extension of the "universal" bond rotation relaxation model to the (110) surface of a highly ionic I-VII compound. CuCl is a large-direct-band-gap semiconductor ($E_g = 3.4$ eV) which crystallizes in the zinc-blende structure, and has the third highest spectroscopic ionicity among zinc-blende compounds ($f_i = 0.746$), below AgI ($f_i = 0.77$) and CuF ($f_i = 0.766$) [2]. It has been studied over the past two decades in view of its peculiar electronic band structure and strong nonlinear optical characteristics [10–14].

The dynamical analysis of low-energy electron-diffraction (LEED) intensities used herein has led, over the past decade, to the determination of the surface structure of numerous semiconductors, several of which have since been confirmed by independent experimental studies [4]. The present structure determination demonstrates that the CuCl(110) surface is relaxed and that the top layer anion-cation displacement normal to the surface is compatible with the scaling law of the universal (110) structure [6]. A secondary effect of ionicity is seen in the contraction of the surface bonds associated with displacements parallel to the surface. The resulting structure is incompatible with that predicted by Tsai *et al.* [7].

CuCl(110) surfaces were obtained by epitaxial growth in ultrahigh vacuum of thin CuCl layers on GaP(110). The lattice mismatch between GaP ($a_0=5.451$ Å) and CuCl ($a_0=5.406$ Å) is ~0.8%. Details on the preparation of the substrate and on the chemistry and band lineup at the CuCl/GaP interface will be given elsewhere [15]. 300-Å-thick CuCl layers were grown by congruent evaporation from a high-purity CuCl powder placed in a quartz crucible. The evaporation rate was 20 Å/min and the substrate growth temperature was 100 °C. Higher substrate temperatures led to faceting and interface reaction, and lower temperatures to poor epitaxy. Smooth CuCl surfaces were obtained, giving sharp (1×1) LEED patterns with the twofold $(hk)=(\bar{h}k)$ symmetry of the (110) unit cell.

The intensity versus energy (I-V) profiles of thirteen nonequivalent diffracted beams, i.e., the (01), $(0\bar{1})$, $(11)=(\bar{1}1)$, $(1\bar{1})=(\bar{1}\bar{1})$, $(10)=(\bar{1}0)$, (02), $(0\bar{2})$, $(12)=(\bar{1}2)$, $(1\bar{2})=(\bar{1}\bar{2})$, $(20)=(\bar{2}0)$, $(21)=(\bar{2}1)$, (03), and $(0\bar{3})$, were recorded in normal-incidence condition in energy steps of 2 eV. In view of the Debye temperature of the material ($\theta_D=180$ K at room temperature [16]), all LEED measurements were taken at 120 K.

The dynamical calculations of the LEED intensities were performed with a multiple-scattering model [17]. The electron-ion-core scattering factors were calculated from a muffin-tin approximation of the crystal potential obtained from overlapping atomic potentials embodying energy-dependent Hara exchange [18]. The energy-dependent Cu and Cl muffin-tin radii, defined by the crossover points of the overlapping potentials, were practically constant in the energy range considered here (30-180 eV) and equal to 1.174 and 1.167 Å, respectively. In the LEED intensity calculations, each atomic layer parallel to the surface was divided into one Cu and one Cl sublattice. The scattering amplitudes for each sublattice were evaluated analytically whereas the scattering between sublattices was described by a set of coupled matrix equations. These equations were solved exactly for the top six layers. For deeper layers, the scattering amplitudes for each layer were obtained by considering the multiple scattering between the two sublattices within the layer but neglecting the multiple scattering between layers. In the calculation, the electron-electron interaction was taken into account via a complex optical potential $\Sigma(E)=-V_0+iV_i$ where V_0 is a constant, real inner potential, and V_i is characterized by the inelastic mean free path λ_{ee}. The fit between experimental and calculated I-V profiles was quantified with the x-ray R factor [19] and the integrated-intensity R factor (R_I) [20]. The latter gives a measure of how the calculation meets the relative strength of various beams. The structure search was performed with six phase shifts. For each calculation, V_0 was selected to minimize R_x with λ_{ee} set at 8 Å. V_0 was always found approximately equal to 9 eV. The thermal lattice vibrations were taken into account in the calculation via an imaginary part of the phase shifts calculated for $u^2(\mathrm{Cu})=u^2(\mathrm{Cl})=0.0306$ Å^2.

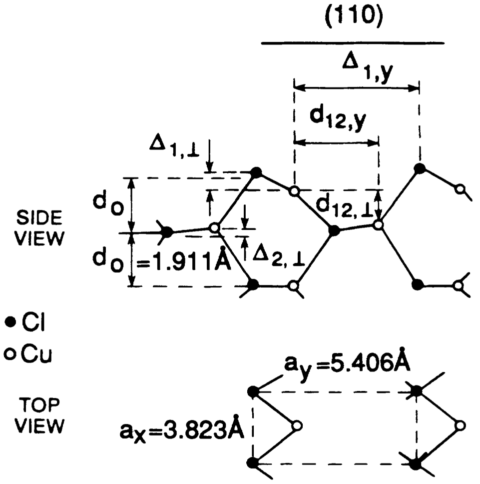

FIG. 1. Side and top view projections of the zinc-blende lattice defining the structural parameters used in the text.

The parameters which describe the geometry of the first two atomic layers of the crystal are defined in Fig. 1. The truncated bulk ("unrelaxed") atomic geometry is specified in the upper row of Table I. This structure was ruled out in view of the very poor agreement it produced on the relative strength of the I-V profiles, as given by $R_I=0.30$. Structural refinements around this unrelaxed geometry did not improve R_x nor R_I. The structure search was expanded by systematically varying all the parameters defined in Fig. 1 until new minima in R_x and R_I were found. The structure was first modified through a bond-length-conserving rotation of the surface Cu-Cl bond, specified by the tilt angle ω with Cl and Cu moving outward and inward, respectively. The constraint on bond length was then relaxed and the top-to-second-layer distance $d_{12,\perp}$ was optimized. ω was reexamined at the optimized $d_{12,\perp}$ value. Finally, $\Delta_{1,y}$ and $\Delta_{2,\perp}$ were varied by independently moving the anion and cation in the top layer parallel to the surface, and in the second layer perpendicular to the surface, respectively.

The geometry which produced the best fit between ex-

TABLE I. Structural parameters of CuCl(110). We give the effective value of ω modified by the Cl horizontal displacement.

Structure	$\Delta_{1,\perp}$ (Å)	$d_{12,\perp}$ (Å)	$\Delta_{1,y}$ (Å)	$d_{12,y}$ (Å)	$\Delta_{2,\perp}$ (Å)	ω (deg)	R_x	R_I
Unreconstructed	0	1.911	4.054	2.703	0	0	0.18	0.30
"Best" fit	0.68 ± 0.05	1.28 ± 0.05	4.6 ± 0.1	3.2 ± 0.2	0 ± 0.05	41.3	0.16	0.06

perimental and calculated *I-V* profiles is given in the bottom row of Table I. It corresponds to a $\omega \sim 30°$ bond-length-conserving rotation of the top-layer bond giving a vertical top-layer shear $\Delta_{1,\perp} = 0.676$ Å, a contraction of the top-to-second-layer distance by 0.15 Å, and an additional 0.4 Å horizontal displacement of the top Cl toward the top Cu. This displacement increases the effective ω to 41.3° (Table I) without, however, modifying the vertical shear $\Delta_{1,\perp}$ corresponding to the 30° bond-length-conserving rotation. The horizontal Cl displacement causes a ~7% contraction of the top Cu-Cl bonds. Finally, no atomic displacements were found in the second (and deeper) layer of the crystal.

The accuracy with which the *R*-factor method determines each structural parameter is obtained according to the criterion that structurally significant differences between experimental and theoretical *I-V* profiles correspond to R_x values that differ by more than 0.02 [21]. The application of this criterion to the present analysis leads to the uncertainties specified in Table I. The CuCl structure produces R_x and R_I values comparable to the best values obtained in our previous studies of cleavage surfaces of III-V or II-VI compounds [4], and can therefore be considered to be established with a high degree of confidence. A comparison between measured and calculated *I-V* profiles of representative diffracted beams is shown in Fig. 2.

The significance of this structure determination is that the (110) surface of CuCl, a I-VII compound with one of the highest spectroscopic ionicities in the zinc-blende family, is relaxed. Moreover, the relaxed structure corresponds to the universal bond rotation structure of (110) surfaces with an additional displacement of the Cl species parallel to the surface. The first-layer vertical shear $\Delta_{1\perp}$, which uniquely defines ω for bond-length-conserving rotations, is the parameter most accurately determined in this analysis by LEED. Its value normalized to the lattice constant is plotted against spectroscopic ionicity in Fig. 3 with those of other III-V and II-VI compounds, and is in excellent agreement with the prediction from the empirical scaling law illustrated by the least-squares fit to the experimental points. It is, however, in disagreement with the prediction of an unrelaxed surface by Tsai *et al.* [7]. The displayed similarity between the $(\Delta_{1\perp}/a_0)$ of CuCl and GaAs or InP indicates that the major features of the surface relaxation of these materials are determined by surface atomic topology rather than by ionicity. It is likely, however, that ionicity plays a role in the details of the surface structure, as evidenced by the 7% Cu-Cl surface bond contraction, the largest such contraction yet found on any (110) surface.

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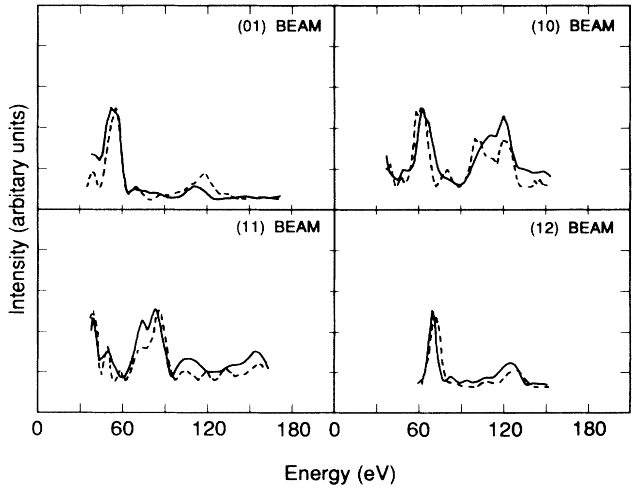

FIG. 2. Comparison between measured (full curve) and calculated (dashed curve) *I-V* profiles of the (01), (10), (11), and (12) beams. The calculation corresponds to the best-fit structure given in Table I.

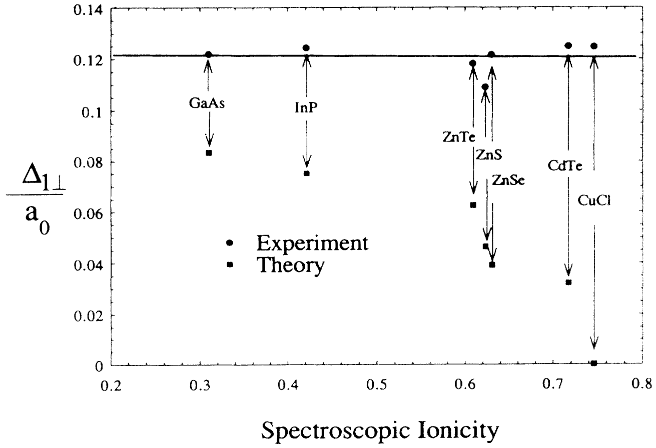

FIG. 3. Comparison of the normalized first-layer vertical shear, $\Delta_{1\perp}/a_0$, corresponding to the best-fit structures obtained from LEED intensity analyses [5] (●) and to the theoretical prediction by Tsai *et al.* [7] (■). The solid line is the best least-squares fit to the experimental values.

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