

SURFACE BOND-LENGTH DETERMINATIONS WITH SHADOW-CONE ENHANCED DESORPTION

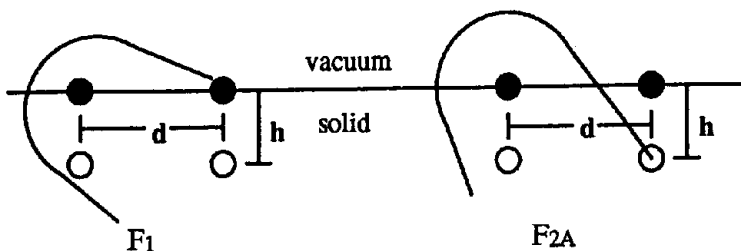
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1. Introduction

We have recently found that the yield of ions ejected due to keV ion bombardment of single crystal surfaces depends on the angle of incidence of the primary ion beam in such a way as to allow simple determinations of surface bond-lengths.¹ With this configuration molecular dynamics calculations indicate that the desorption yield of all particles is significantly enhanced when the shadow-cone of the incident beam of particles created by a surface atom intersects adjacent surface or sub-surface atoms.² There are several bombarding geometries that lead to the enhanced yield. On clean Ag{110}, for example, we find maxima in the yield corresponding to the intersection of a Ag shadow-cone with an adjacent surface atom, type F₁ and with an adjacent second-layer atom, type F_{2A}. Using only the known shadow-cone shape and the measured



yield maxima, we are able to compute the distance h or d to a precision of $\pm 0.05 \text{ \AA}$ in favorable cases. So far we have utilized this method to examine surface relaxation on clean Ag{110}² and have measured the Ag-Cl bond-length of Cl adsorbed on Ag{110} as a function of coverage.^{1,3} In the latter case, using the F_{2A} mechanism, we find that the Ag-Cl bond-length changes from an extended value of 2.90 \AA at very low coverage to nearly 2.50 \AA at the 1/2 monolayer (ML) point. The latter value is in good agreement with surface extended absorption fine structure (SEXAFS) experiments recently performed on this system.⁴

In this paper, we report on shadow-cone enhanced desorption experiments on Ag{001} reacted with Cl₂. For the c(2x2) low energy electron diffraction (LEED) structure, we find that the Ag-Cl bond-length is 2.61 Å, again in excellent agreement with LEED⁵ and SEXAFS⁶ experiments. Based on azimuthal angle studies we also show that at room temperature the Cl binds in a simple overlayer model (SOM) arrangement, but at higher temperatures, the surface converts to a mixed layer model (MLM) where an epitaxial layer of AgCl forms on top of Ag{100}.⁷

2. Experimental and Computational Procedures

The ultrahigh vacuum experimental apparatus has been described previously.¹ Shadow-cone enhanced desorption was detected using a 2 or 3 keV incident Ar⁺ ion beam under low dose (static) conditions. Either Ag⁺ or Cl⁻ ions were desorbed into a movable Riber Q156 quadrupole mass spectrometer. The angle of incidence, θ_i , the detection angle, θ_d , and the angle between the mass spectrometer and the ion gun, β , could be varied independently. Shadow-cone shapes were determined using a Moliere potential. The Firsov screening factor was calculated using previously developed empirical formulae to be 1.03 for Ar-Ag and 0.86 for Ar-Cl.⁸ The position of the shadow-cone edge was defined by the locus of turning points resulting from a series to two-body trajectory calculations.

3. Results and Discussion

The azimuthal angle distributions for Cl⁻ and Ag⁺ for Cl on Ag{001} are shown in Fig. 1. Note that the Ag⁺ ions are significantly blocked by Cl overlayer atoms. The shape of these curves uniquely places the Cl atom in the 4-fold hollow site of the Ag{001} surface. The shadow-cone desorption spectra for Ag⁺ and Cl⁻ are shown in Fig. 2. The F_{2A} peak at 28° for Cl⁻ corresponds to a Ag-Cl bond-length of 2.61 ± 0.05 Å. The peak at higher angles is a complicated mixture of Ag and Cl shadow-cones and is not usable in a quantitative fashion at the present time. Note that the F_{2A} peak is independent of the angle β for Cl⁻ but not for Ag⁺. The β independence is only expected if desorbing ions arise from the topmost layer, as for Cl desorbing from the c(2x2) structure with Cl in the 4-fold hollow site. The β dependence of the Ag desorption arises from channeling and blocking effects of the overlayer Cl and is indicative of ejection from below the surface plane.

This idea can be quite important. As seen in Fig. 3, when the c(2x2) structure is heated to 380°C, the Ag⁺ and Cl⁻ exhibit an F_{2A} peak at the same angle and at the same angle as for the SOM. This result strongly suggests that *both the Ag and the Cl are in the topmost layer* and that an epitaxial layer of AgCl has indeed formed. This structure, termed the MLM, has long been postulated but never confirmed.⁷

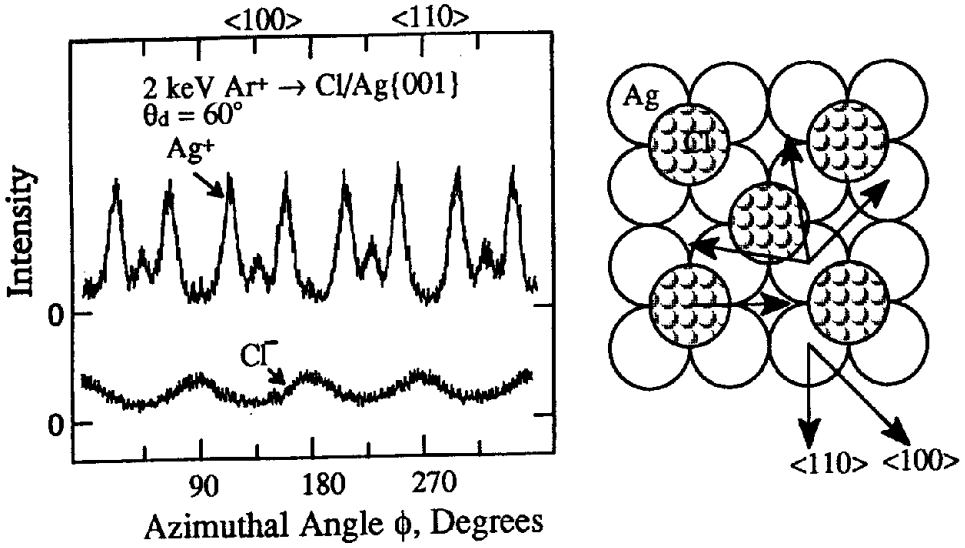


Fig. 1. Azimuthal angle distribution for $c(2 \times 2)$ -Cl/Ag(001) with a polar detection angle of $\theta_d = 60^\circ$. Note the excellent 4-fold symmetry, the effects of Cl blocking on the Ag^+ distributions and the effects of Ag channeling on the Cl^- distributions.

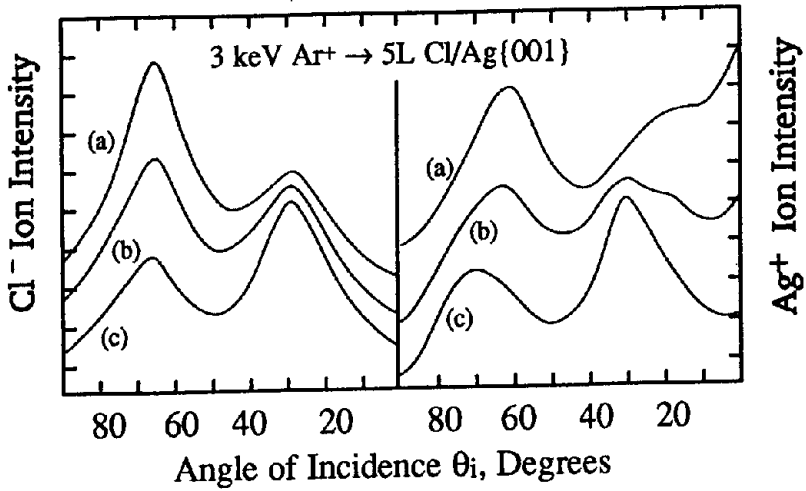


Fig. 2. Yield as a function of angle of incidence for Cl^- and Ag^+ ions from $c(2 \times 2)$ -Cl/Ag(001); (a) $\beta = 45^\circ$, (b) $\beta = 35^\circ$ and (c) $\beta = 25^\circ$.

IV. Conclusions

Angle-resolved SIMS with shadow-cone enhanced desorption is potentially a very powerful surface-structure tool. Our results here show that with a very simple set-up bond-lengths may be determined rather accurately. It will be most interesting to see how generally this method can be applied to new types of surface structure

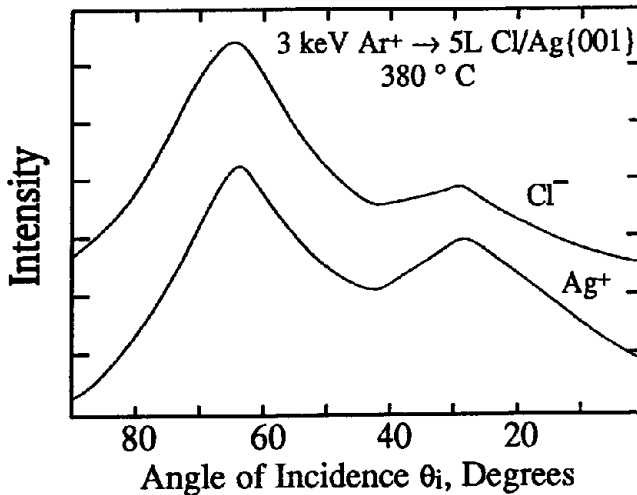


Fig. 3. Yield as a function of angle of incidence for Ag⁺ ions and Cl⁻ ions from c(2x2)-Cl/Ag(001) after heating the room temperature sample to 380°C. In this case, $\beta = 45^\circ$.

problems, particularly due to its high sensitivity and experimental ease of use.

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4. References

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