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Absolute coverage of cesium on the Si(100)-2×1 surface

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He^+ Rutherford backscattering spectrometry has been applied to measure the absolute saturation coverage of Cs on the Si(100)-2×1 surface at room temperature. The measured Cs saturation coverage is 0.54 ± 0.02 monolayers (ML) [1 ML is the density of surface atoms for bulk-terminated Si(100), or 6.78×10^{14} atoms/cm^2]. This result supports structural models requiring a Cs coverage of 0.5 ML and refutes several alternative models.

Alkali-metal adsorption on semiconductor surfaces has been investigated over many years for both theoretical interest and technological applications. Early research was motivated by the discovery that the Cs/Si(100)-2×1 system exhibits negative electron affinity (NEA)—a state where the conduction-band minimum extends above the vacuum level. Interest in the manufacture of low-temperature and low-field electron emission sources prompted investigation into the mechanisms that produce the NEA band alignment.[1,2] More recently, it was discovered that alkali metals adsorbed on Si surfaces catalyze the growth of silicon dioxide.[3] There is, therefore, potential for their use in the manufacture of high-quality silicon dioxide insulating layers for semiconductor devices. (Cesium is particularly promising in this regard since it causes minimal disruption of the silicon surface. In addition, Cs is easily desorbed, thus eliminating contamination concerns associated with the lighter alkali metals.[4]) The simple valence-band structure of alkali metals is useful for modeling metal-semiconductor interface properties from the initial stages of adsorption, through interfacial metallization, and on to the formation of multilayer, metallic films.

Knowledge of the detailed structure of the alkali-metal atoms on the semiconductor surface is essential for understanding the early stages of metallization. For an ordered structure in a single-particle picture, simple electron counting predicts whether or not the overlayer will be metallic. However, it has been shown that even for submonolayer coverages electron correlation effects can be significant.[5]

Past studies of alkali-metal adsorption in the monolayer regime have focused on bonding site(s), atomic structure, and electronic properties, but they have largely addressed coverage only incidentally. In most cases, coverage has been inferred indirectly by assuming a structural model for which data are consistent. For example, diffraction data must be compared with a small number of ordered adsorption site models in the hope that one is a match to the system. Similarly, desorption measurements produce information on bonding states, but not direct information on coverage. Measurements of adsorbed alkali metals by scanning tunneling microscopy (STM) have been problematic due to tip-surface interactions and the difficulty in decoupling atomic and electronic structure in real space. In this work, a direct approach to measuring the absolute coverage of a saturated Cs layer has been taken using Rutherford backscattering spectrometry (RBS).

Goldstein and Levine were among the first to study the saturated Cs/Si(100)-2×1 interface.[1,2] Based on their low-energy electron diffraction (LEED) and Auger electron spectroscopy (AES) studies of the interface and its oxide, they proposed the model illustrated in Fig. 1(a) in which Cs atoms are adsorbed along the dimer rows of the Si(100)-2×1 surface. The model has a Cs saturation coverage of 0.5

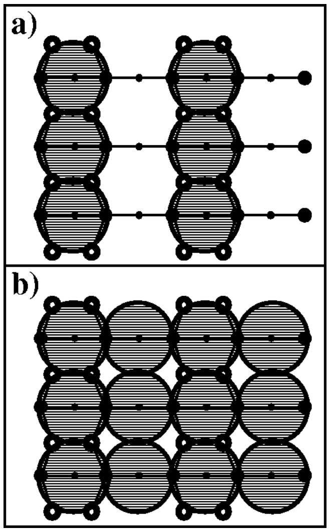

FIG. 1. (a) The Levine model of the Cs/Si(100)-2×1 interface with 0.5 ML of Cs (Ref. 2) (b) The Abukawa and Kono model of Cs/Si(100)-2×1 showing 1 ML of coverage (Ref. 6). Gray Cs atoms are shown (scaled to the silicon lattice) with a radius of 2.02 Å, which is the average of the covalent and ionic radii [this is a sensible representation given that Soukiassian *et al.* (Ref. 9) found the Cs/Si bond to be covalent but polarized].

monolayers (ML), where 1 ML is defined as the density of surface atoms for bulk-terminated Si(100), or 6.78×10^{14} atoms/cm^2. Simple electron counting for this coverage predicts a half-filled band crossing the Fermi level, which is consistent with a metallic surface in a single-particle picture.

Later, Abukawa and Kono proposed a different model, shown in Fig. 1(b), that was based on their x-ray photoelectron diffraction measurements[6] as well as an earlier report of semiconducting behavior for the interface.[7] In this model, Cs atoms are adsorbed on the silicon dimer rows (similar to the Levine model) and in the valleys between the dimers. The resultant Cs saturation coverage of 1 ML has two Cs valence electrons per unit cell, which is consistent with semiconducting behavior.

There may be concern that the structural models shown in Fig. 1 are not plausible based on steric grounds. The nearest Cs-Cs distance for these structures is 3.84 Å, which is small when compared to the Cs nearest-neighbor distance of 5.30 Å for bulk cesium[8] or to the covalent-bonding diameter for Cs of 4.70 Å.[8] The spacing is, however, greater than the 3.38 Å Pauling ionic diameter of Cs,[8] which suggests that the Cs/Si bond is ionic. This was contradicted by core-level and valence-band photoemission spectroscopy measurements of Soukiassian *et al.*[9] Initially debated in the literature,[10–12] they suggested that the Cs 6*s* and Si 3*p* states hybridize to form a localized, polarized covalent bond. In Fig. 1, we show that it is possible to accommodate the ~3.84 Å Cs-Cs distance in the previously proposed models if the Cs radius is taken to be intermediate between the ionic and covalent radii (or if there are small shifts in/out of the plane as proposed by Abukawa and Kono[6] and by Meyerheim and co-workers[13]).

Several other studies have been directed at resolving the geometric and electronic structure of the Cs/Si(100) system.[14,15] However, these measurements have not yet resolved the issue of structure or the more fundamental issue of Cs coverage. Scanning tunneling microscopy has the potential to directly view structure; however, Xu, Hashizume, and Sakurai reported that STM failed to image the Cs clearly because the highly reactive overlayer easily modified the scanning tips.[16] The thermal desorption spectroscopy of Kennou *et al.*[17] suggested the existence of two Cs adsorption sites, which was regarded as support for the 1 ML Abukawa and Kono model.[6] However, based on uptake rate calculations, they concluded that the saturation Cs coverage is only 0.75 ML. The core-level photoelectron spectroscopy studies of Chao, Johansson, and Uhrberg[12] suggested the existence of two binding sites (as predicted by Abukawa and Kono), but metallic behavior was observed (as per the Levine model).[2] Taken altogether, these observations are at variance with the Abukawa and Kono model. Tensor LEED analyses gave support to the Abukawa and Kono model.[15,18] A subsequent surface x-ray diffraction analysis by Meyerheim and co-workers[13] suggested the existence of several partially occupied binding sites. They proposed a structural model with nonsymmetric Cs binding sites and a coverage of 0.3 ML; this structural model was not considered as a possibility for the Tensor LEED analyses.[15,18] In addition, a proton-beam RBS study has been reported concluding that the saturation coverage is 0.97 ± 0.05 ML.[19] This result was called into question, however, over concern that the proton beam might promote excess cesium adsorption.[20] Thus even after numerous studies the room-temperature saturation coverage of Cs on Si(100)—a crucial factor in determining the structure—remains unresolved.

An accurate independent coverage measurement is the key parameter to confirm the plausibility of a structural model. For comparison with measurements that rely on structural order, the measured absolute coverage provides a reliable upper limit on the coverage related to the coherent fraction. For these purposes, He-beam RBS is an ideal direct probe of Cs coverage for the saturated Cs/Si(100)-2×1 interface. The cesium overlayer and the silicon substrate are easily distinguished, and the use of nonreactive He eliminates concerns associated with hydrogen-beam RBS studies. Furthermore, unlike many other techniques, RBS does not depend on any structural or binding site model for analysis; thus it is a direct probe of the absolute coverage of the adsorbed layer.

The experiments were performed in an ultrahigh vacuum (UHV) analysis chamber attached to a Van de Graaff ion accelerator by a differentially pumped beam line. The experimental chamber houses AES and LEED systems as well as a solid-state ion detector for RBS AES and LEED systems. The base pressure of the chamber is less than 2×10^{-10} torr. Silicon samples were cut from polished *n*-type wafers ($\rho \approx 5\ \Omega$ cm), mounted onto a sample holder with molybdenum clamps, and transferred into the analysis chamber through a load lock onto a high-precision goniometer. The sample and holder were outgassed for ~48 h at a temperature of ~150 °C to ensure a clean and contaminant-free environment for subsequent high-temperature annealing. The surface oxide layers were removed from the as-introduced samples using a standard procedure[21] in which the Si is resistively heated to ~1100 °C and then cooled slowly to room temperature while a pressure less than 2×10^{-9} torr is maintained. This procedure effectively removes the surface oxide while avoiding surface roughening. Auger spectra of surfaces prepared in this manner exhibited no detectable traces of oxygen, carbon, or any other minor contaminants. LEED displayed two-domain 2×1 diffraction patterns, as expected. Cs depositions were subsequently performed on the cleaned samples at room temperature.

Cs was deposited from a well-outgassed SAES chromate getter source mounted ~2 cm from the sample. The work function change ($\Delta\Phi$) and Cs/Si AES intensity ratio reached plateaus after ~11 min exposure times. $\Delta\Phi$ at saturation coverage was measured to be -2.4 ± 0.2 eV, which is comparable to other published results that have reported values between -2.6 and -3.25 eV.[2,12,22] To ensure a saturated Cs surface layer for our RBS measurements, dosing times were typically extended to 20–30 min. Upon reaching saturation Cs coverage, the characteristic 2×1 LEED pattern was still observed with a slightly increased background.[2] AES analyses after Cs exposures indicated that cleanliness was satisfactorily maintained; the maximum O and C number densities were each much less than 5%.[23]

The RBS measurements were made using a recently commissioned ion beam line on the University of Pennsylvania NEC 1.7 MV tandem Van de Graaff accelerator. The beam is collimated by two apertures that limit its divergence to less than 0.5°. The first 93-mm-diameter aperture is 110.5 cm

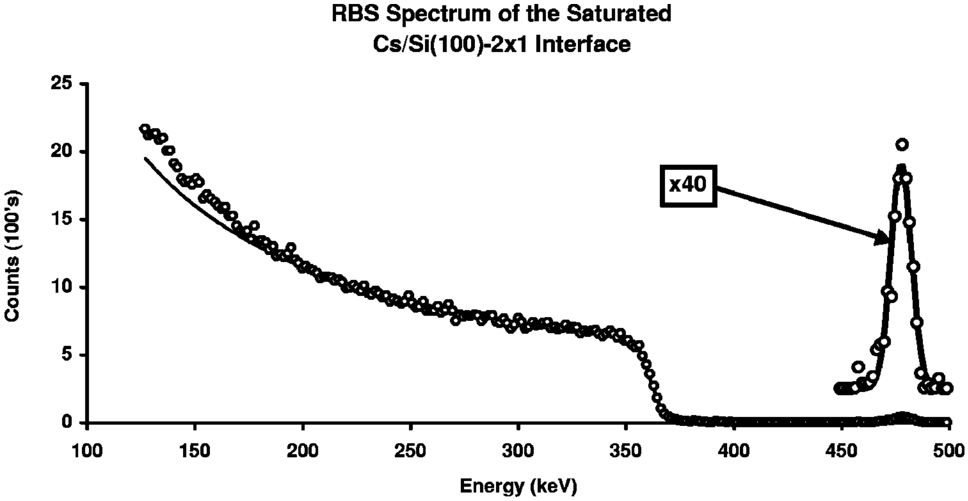

FIG. 2. RBS spectrum (incident angle 50.1°, $E=510\,\mathrm{keV}$) for saturated Cs/Si(100)-2×1 showing data (circles) and simulation (line). The height of the silicon shoulder and the distance between the shoulder and the cesium peak (enlarged at right) are fitted to assure correct calibration.

from the sample, and the second rectangular ($1.23\times0.616\,\mathrm{mm}^2$) aperture is positioned 9 cm from the sample. Pumps mounted in the beam line allow the pressure in the analysis chamber to be maintained in the 10^{-10} torr range when open to the accelerator.

RBS measurements were made using a $^4\mathrm{He}^+$ beam at a kinetic energy of ~500 keV. The energy of the recoiling ions was measured by a bakeable Canberra passivated implanted planar silicon detector set at a fixed scattering angle of 104°. To avoid ambiguities in the analysis due to possible shadowing effects, data were collected for several angles of incidence between 35° and 50°. The data were collected by a multichannel analyzer/personal computer system and analyzed by comparing the experimental RBS spectra to simulations obtained from a commercial software package.[24] In the analysis, the energy scale and the total charge incident on the sample were independently obtained because the silicon signal is virtually undisturbed by an atomically thick Cs surface layer and the position of the Cs peak is a known function of scattering geometry. An independent check of the system to assess experimental error was performed by analyzing an Sb-implanted Si calibration standard with an Sb concentration known within ±2%. From this analysis, the experimental accuracy of a Cs coverage measurement with high counting statistics was determined to be ±3%.

Figure 2 shows a typical RBS spectrum with a best-fit simulation. Since the simulation does not consider multiple scattering, it underestimates the scattering intensity in the lower-energy region (<200 keV) by up to ~5%. It is, however, accurate at the higher-energy region of the spectrum (>200 keV) upon which our measurements depend.[25]

A detailed analysis of the Cs peak from Fig. 2 is presented in Fig. 3. The error bars are based on the statistical uncertainty $1/\sqrt{N}$. For this run, the best-fit simulation (black line) gives a Cs saturation coverage of $0.47\pm0.04\,\mathrm{ML}$. A weighted average of measured coverages obtained from several samples and depositions results in a best value for the Cs saturation coverage of $0.54\pm0.02\,\mathrm{ML}$.

It is important to note that RBS analysis is based only on known ion scattering cross sections that are dependent on ion impact energy, ion mass, and scattering geometry. Thus, these results are completely independent of any particular structural model for Cs adsorption. The absolute coverage determination we have made limits the possible surface structural models to those consistent with ~0.5 ML Cs coverage. A 1 ML coverage, corresponding to the structural model of Abukawa and Kono,[6] is also simulated in Fig. 3 and shown to be inconsistent with our data.

We have found the effects of residual contamination on surface coverage to be extremely small. Careful analysis of samples where the O/Si AES intensity ratios were 2–8 % (using a 3 keV incident electron beam) suggests that the Cs saturation coverage obtained with RBS is independent of O contamination within experimental uncertainty. In contrast, Cs saturation coverage was significantly affected (uptake to ~1.25 ML) for instances where the O/Si AES ratio was intentionally increased to ⩾10%, more than twice the oxygen concentration for samples considered in our analyses. This

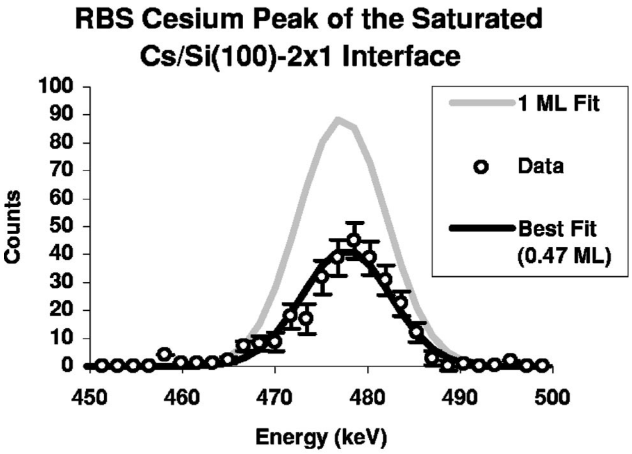

FIG. 3. Detail of cesium peak from Fig. 2 showing data (circles), a best-fit simulation of 0.47 ML of cesium (black line), and a simulation of 1 ML predicted by the Abukawa and Kono model (Ref. 6) (gray line).

suggests that any errors caused by oxygen contamination could only slightly increase the observed cesium coverage.

In summary, helium-beam RBS measurements were carried out on a newly commissioned UHV ion-beam surface analysis system. The absolute saturation Cs coverage on the Si(100)-2×1 surface was determined to be 0.54 ± 0.02 ML. This absolute coverage measurement imposes a definitive upper limit on acceptable structural models. In particular, the data are consistent with models based on 0.5 ML saturation Cs coverage, such as the Levine model.[2] These data are not consistent with models predicting Cs saturation coverages greater than 0.5 ML.

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