Cs and O adsorption on Si(100) 2×1: A model system for promoted oxidation of semiconductors

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(Received 6 July 1987)

We present Auger-electron spectroscopy, low-energy electron diffraction, and $\Delta\phi$ measurements of Cs adsorption on Si(100) and subsequent oxidation of the substrate. Our data provide evidence against complete charge transfer from the alkali metal to Si as proposed recently. The amount of SiO₂ produced by alkali-metal-promoted low-temperature oxidation of silicon is found to be strictly proportional to the alkali-metal coverage, which, together with measured changes in the work function during oxidation, allows us to question some of the current mechanisms put forward to explain this phenomenom.

The study of alkali metals deposited on the surface of semiconductors is a field of enormous interest. Since the seminal works of Weber and Peria,^{1,2} photocathodes, infrared detectors,³ or spin-polarized electron guns⁴ have been produced on the basis of the knowledge acquired on various alkali-metal-semiconductor combinations. Very recently there has been a renewed interest in this topic brought about by the possibility of using intralayers of al-kali metals between two semiconductors in order to modify by band-gap engineering the band-gap discontinuity in superlattices,⁵ and by the spectacular promoter effect of alkali metals in low-temperature oxidation of Si.⁶⁻⁸

In this latter field it has been shown that careful studies of the mode of growth of K on $Si(100)2 \times 1$, the electronic structure, the charge transfer, and the work-function changes were a crucial prerequisite to understanding the enhanced oxidation of Si produced by subsequent O₂ exposure.⁹ Recently, there have been some suggestive calcula-tions on charge-transfer metallization^{10,11} as well as reports of strong enhancement in the oxidation rate^{7,8} for the closely related CsSi system. In this case, however, an experimental characterization that can provide a firmer basis for detailed models was lacking. The purpose of this Rapid Communication is to present experimental data for C on Si(100)2×1 that describe the alkali adlayer prior to oxygen adsorption, as well as the subsequent oxidation process as a function of the Cs coverage. The data indicate that (i) the charge transfer from Cs to Si at completion of the Cs adlayer is not complete, (ii) the average work function increases upon oxygen adsorption, and (iii) the amount of SiO₂ produced is proportional to the coverage of Cs on the surface prior to oxygen adsorption. Our data do not support current ideas about alkali-metalsemiconductor interaction 10,11 and enhanced oxidation of Si.^{7,8}

The measurements were performed in an ultrahigh vacuum chamber⁹ with a base pressure of 10^{-10} Torr during Cs deposition. the Si(100) sample, cut from a commercial wafer (*n* doped, 30-50 Ω cm), was cleaned running through cycles of Ne⁺ ion bombardment and heating to 1100 K. Prior to Cs adsorption it showed a good 2×1 low-energy electron diffraction (LEED) pattern. Cs was evaporated by means of a heated dispenser (SAES Getters). The LEED pattern was obtained with a fourgrid optics, the Auger-electron spectroscopy (AES) data through a 2 V peak-to-peak modulated single-pass cylindrical mirror analyzer (CMA), and the work-function changes by means of a Kelvin probe.

Figure 1 shows the peak-to-peak intensity of the Si *LVV* Auger transition of 92 eV and the Cs *NOO* transition at 47 eV as a function of the Cs evaporation time at 200 K. Breaks are observed in the time evolution of both Cs and Si peaks. These breaks may correspond to completion of successive layers or to sudden changes in the sticking coefficient.⁹ At the first break, the attenuation coefficient of the Si signal due to the Cs overlayer is 0.59. Taking the theoretical expressions for layer-by-layer growth,⁹ the corresponding inelastic mean free path (IMFP) of Si Auger electrons is $\lambda = 2.5$ ML (ML denotes monolayers) in agreement with previous results for K/Si(100).⁹

In order to determine the Cs coverage at this break additional information is required. The LEED pattern demonstrates that the 2×1 (two domains) symmetry of the clean Si(100) surface is unchanged upon deposition of this amount of Cs. The intensity distribution in the spots, however, differs from the clean surface. In analogy with the K/Si(100) system⁹ the simplest choice is to assume that at this coverage Cs atoms form chains along the [110] direction. The rows are 7.68 Å apart along the $[1\overline{1}0]$ direction. The density of surface atoms in $Si(100)2 \times 1$ is 6.78×10^{14} atoms/cm². Thus, the Cs coverage at this point is taken to be $\Theta = 0.5$ ML, i.e., $n_a = 3.39 \times 10^{14}$ atoms/cm². It should be noticed that the density of the (110) plane in metallic Cs is 3.86×10^{14} atoms/cm². Total-energy calculations¹⁰ and scanning tunneling microscopy (STM) images of the unoccupied surface states on $Si(100)2 \times 1$ taken by Tromp, Hamers, and Demuth¹² suggest that Cs atoms might be located in the fourfold hollow site between two dimers. A side view of the proposed geometry is depicted in the inset of Fig. 1. In this geometry the radius of Cs is 1.92 Å, noticeably smaller than the covalent radius of 2.35 Å but still above the ionic radius of 1.69 Å.

Further adsorption of Cs results in a layer-by-layer growth of the deposit. The rise in intensity of the Cs signal yields an IMFP value for Cs Auger electrons of

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FIG. 1. Peak-to-peak intensities of the Si and Cs Auger transitions at 92 and 47 eV, respectively, as a function of the evaporation time for Cs on Si(100). The data were taken at 200 K. Notice that the initial value of the Cs peak is not zero because of a feature in the spectrum of clean Si at the same kinetic energy.

 $\lambda_{\rm Cs}$ = 1.3 ML. The reduced value of the escape depth in Cs, also found in photoemission,¹³ produces only a small increase of the Cs AES signal with evaporation time that has been mistaken as a sign of zero sticking coefficient in the past.¹⁴ Actually, for Cs coverages between 0.5 and 1 ML the sticking coefficient of Cs at 200 K drops to 0.67 as suggested by the longer time, at constant evaporation rate, needed to reach the second break which corresponds to $\Theta = 1$ ML. A further decrease of the sticking coefficient to 0.28 occurs for the second layer of Cs.

It is commonly stated in the literature that Cs adsorption on metal or semiconductors results in a maximum coverage at room temperature of 1 ML.^{8,10,14} However, this sentence only indicates that 3D growth is not observed. The saturation coverage in equilibrium at 300 K has not been properly determined. The calibration at low temperature shown in Fig. 1 allows us its determination. Room-temperature adsorption of Cs on Si(100)2×1 results in a Cs/Si Auger peak ratio of 0.65 at saturation, i.e., 0.78 ML or 5.3×10^{14} atoms/cm².

Figure 2 depicts the work-function changes observed during deposition of Cs on Si(100). The contact potential difference (CPD) versus coverage curve shows a maximum decrease of -3.4 eV, corresponding to a minimum value of the work function of 1.45 eV. AES spectra taken at this minimum indicate that it corresponds to the first break in the Auger versus evaporation time curves, i.e., to completion of the Cs chains at a coverage of $\Theta = 0.5$ ML. As further Cs atoms are adsorbed the work function rises to a saturation value of $\Delta \phi = -2.8$ eV. This corresponds to a work function of ≈ 2.0 eV for a complete monolayer of Cs in comparison to the Cs bulk value of 1.8 eV.

In the case of semiconductors the CPD measured by the Kelvin probe equals $\Delta \phi = \Delta I - e \Delta V_B$ where ΔI is the

change in ionization energy and V_B is the band-bending change (ΔV_B is positive for upwards band bending). Accordingly, the work function can be reduced by both an adsorbed dipole layer at the surface and by a downwards band bending, i.e., a displacement of the conduction-band edge at the surface towards the Fermi level. Si(100)2×1 surfaces prepared by ion sputtering and annealing contain a large density of extended surface defects visualized by STM¹⁵ which produce a metallic density of states at the Fermi level.¹⁶ Consequently no change in band bending is detected upon Cs adsorption¹³ and then work-function changes are due only to changes in the ionization energy.

The lowering of the work function produced by a plane of dipoles is given by the Helmholz equation $\Delta\phi(\Theta)$ = $\sigma\Theta\mu(\Theta)\epsilon_0$ where $\mu(\Theta)$ is the coverage-dependent di-



FIG. 2. Work function change for deposition of Cs at 200 K vs evaporation time.

pole moment, σ is the density of surface sites, and Θ , the coverage. A number of phenomenological models have been developed to derive analytical expressions for relating work function with surface coverage. Among them, the Topping model, ¹⁷ which assigns the decrease of $\mu(\Theta)$ with Θ to self-depolarization of the adsorbed layer, is known to reproduce the experimental data rather well.¹⁸ Topping calculated the reduction in the work function produced by a plane array of mutually interacting, parallel, dipoles of equal dipole moment, μ_0 , as a function of coverage as

$$\Delta\phi(\Theta) = \frac{\sigma\Theta\mu_0}{\epsilon_0 \left| 1 + 9\alpha(\sigma\Theta)^{3/2} \right|} ,$$

where α is the effective polarizability of the adsorbatesubstrate complex. Thus, a plot of $\Theta/\Delta\phi(\Theta)$ vs $\Theta^{3/2}$ should yield a straight line of slope $9\alpha\epsilon_0\sigma^{1/2}/\mu_0$ and intercept $\epsilon_0/\sigma\mu_0$. The experimental data fit nicely a straight line yielding a dipole moment $\mu_0 = 4.12$ D and a polarizability $\alpha = 9.8$ Å³.

The charge transfer between Cs and Si cannot be uniquely determined from the $\Delta \phi$ values. An independent determination of the dipole length is required. However, reasonable estimates can be done easily. The amount of charge donated by the Cs atoms to the surface states of Si can be written as $Q(e/cm^2) = 5.53 \times 10^{13} \Delta I(eV)/L_{eff}(Å)$ where ΔI is the reduction in ionization energy given by $\Delta \phi$ measurements and L_{eff} is the effective dipole length. By taking I = -3.4 eV and $L_{\text{eff}} = 1.92$ Å (effective radius of Cs) a value of $Q \approx 9.8 \times 10^{13}$ e/cm² is obtained. At the minimum of $\Delta \phi(\Theta)$, the coverage of Cs is 3.39×10^{14} atoms/cm² and therefore each Cs atom has transferred ≈ 0.28 electrons to the Si surface states. An independent estimation of the charge transfer can be obtained following Pauling's concept of a relationship between electronegativity and ionic character of chemical bonds.¹⁹ The charge transfer is given by $q/e \approx 1 - \exp(-0.25 |\Delta \chi|)$ where $\Delta \chi$ is the difference of the electronegatives of Si(1.9) and Cs(0.7) in the Pauling scale. This argument indicates that Cs donates ≈ 0.24 electrons per atom to the Si atoms in excellent agreement with the estimation above. This partial transfer of charge is further supported by the results of self-consistent tight-binding calculations²⁰ which demonstrate that charge transfer of a complete electron as proposed by Ciraci and Batra^{10,11} does not occur for 0.5 ML of Cs on Si(100).

As already mentioned, an enhancement in the oxidation rate of Si was observed when the Si substrate was covered by either multilayers of K (Ref. 6) or 1 ML of Cs or Na (Refs. 7 and 8) prior to oxygen adsorption. In the case of K multilayers it has been shown that the amount of oxide produced is proportional to the K coverage.⁶ A mechanism has been proposed based on the trapping of oxygen molecules by the K film and their transfer to the Si substrate upon annealing.⁶ On the other hand, the increase in the oxidation rate detected for 1 ML of Cs on Si(100) has been assigned to dipole-moment-induced enhanced dissociation of O₂ molecules.^{7,8} Furthermore, it was claimed that Si oxidation does not slow down rapidly with O₂ exposure, i.e., a truly catalytic behavior. In order to justify this, it was argued that the Cs-Si surface dipole responsible for the initial oxidation would be replaced by an equally effective Cs-O surface dipole upon oxygen adsorption.⁷ We will show that both assumptions, i.e., constant dipole moment and sustained oxygen rate are not supported by our experimental results.

The adsorption of O_2 on Si surfaces precovered with coverages of Cs provokes changes in the work function as shown in Fig. 3. The origin is taken at the work function of each Cs-covered Si surface. In general, the work function increases, i.e., the average surface dipole decreases, upon oxygen admission. Only for Cs coverages above $\Theta = 0.5$ ML and O_2 exposures below ≈ 0.8 L an additional decrease of the work function is observed. An absolute minimum value of the work function of 0.85 eV occurs for $\Theta = 1$ ML and O_2 exposures of 0.4 L. In any case, the average work function is well above its value for Cscovered substrates at O_2 exposures (10-400 L) of interest for the oxidation reaction (see below).

We interpret the additional lowering of the work function as due to negate oxygen ions adsorbed below the Cs plane. Further support to this interpretation comes from the fact that the Auger emission of Cs increases by $\approx 50\%$ upon oxygen adsorption most probably due to back scattering of the Cs Auger electrons by the negatively charged oxygen ions. In all the other cases the observed increase in the work function is interpreted as due to oxygen adsorbed above the surface plane. These data prove that the Cs-Si surface dipole is not replaced by an equally large Cs-O surface dipole which therefore cannot be equally effective in dissociating O2 molecules. Thus, our findings do not support the model by Franciosi and coworkers.^{7,8} Actually, we do not find evidence of SiO_2 formation in quantities exceeding many times alkali stoichiometry as would be produced by a nonpoisoned catalyst. On the contrary, there is a strict proportionality between the deposited number of Cs atoms and the oxygen uptake indicating a short-range effect.

An overall view of the alkali-metal-promoted oxidation process is given in the right half of Fig. 4. The AES spectra shown correspond to adsorption of Cs on Si(100) followed by oxygen exposure at 300 K and annealing to 900 K. The oxygen adsorption on Cs-covered samples occurs



FIG. 3. Work-function change vs oxygen exposure (1 L $= 10^{-6}$ Torrs) for different Cs-covered Si(100) surfaces. The data have been taken at 200 K. The symbols refer to different Cs coverages. Note that the curves have been shifted to a common origin by the different work function of each Cs-covered Si surface.

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FIG. 4. The right part shows Auger spectra corresponding to the different steps needed to achieve alkali-metal-promoted oxidation of Si. From above to below they correspond to the Si(100) surface clean, covered with 0.5 ML of Cs, exposed to 200 L of O_2 at 300 K and annealed to 900 K, respectively. The left part shows the ratio of the Auger peak-to-peak intensities of SiO₂ (76 eV) and Si (92 eV) from samples which have passed through the process described above as a function of the initial Cs coverage.

with a sticking coefficient almost unity. In agreement with previous observations⁶⁻⁸ the kinetics of oxygen adsorption on Cs-covered surfaces is a factor of 10^5 faster than on clean Si surfaces. The alkali-metal adlayer is desorbed by heating at 900 K, which results in a layer of SiO₂ left on the surface. The thickness of the resulting SiO₂ layer is plotted in the left part of Fig. 4 as a function of the initial Cs coverage.

A linear dependence between the amount of oxide produced and the Cs coverage is obtained. Furthermore, this strict proportionality is independent of the processing method. For a fixed coverage of Cs, the *same* amount of oxide is produced either by exposing continuously to O_2 until the SiO₂ production rate becomes negligible or by exposing to 400 L of O_2 and heating to desorb the Cs. In this case there is a noticeable SiO₂ production during annealing while in the first case heating the adlayer to desorb Cs does not produce more oxide. The total amount

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of SiO_2 is, however, identical in both cases within the experimental error. These facts and the linear increase of the oxidation activity with small amounts of alkali-metal additives can be taken as an indirect indication for a *local* promoter effect in the vicinity of the alkali-metal atoms. We tend to believe that the promoter effect is related to local electrostatic effects rather than to the average work function as will be illustrated in a forthcoming publication.²¹

We thank Dr. Laubschat for help with the experiments. One of us (J.E.O.) thanks Eusko Jaurlaritza for financial assistance. Another of us (J.F.) wishes to thank the Consejo Nacional de Investigaciones Científicas y Técnicas de Argentina for financial assistance. Financial support from the U.S.-Spanish Committee under Grant No. CCA/84-063 is gratefully acknowledged.

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