Charge Exchange in Li Scattering from Si Surfaces

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Neutral fractions are measured for 4 keV $^7Li^+$ scattering from clean, hydrogen-covered, and cesiated Si surfaces. The neutral fraction in scattering from clean Si is ~26% and it decreases with hydrogen adsorption. When Cs is adsorbed on Si, the neutral fraction does not distinguish the local potential at the Cs sites from the Si sites, unless hydrogen is coadsorbed. These results demonstrate that resonant charge transfer occurs due to coupling of the Li ionization level with the dangling bond surface states, and that the influence of the dangling bonds extends beyond the local scattering sites.

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Charge exchange plays a key role in many static and dynamic processes at solid surfaces, as well as in various applications such as secondary ion mass spectroscopy, reactive ion etching, and catalysis. Charge transfer is significant in alkali atom interactions with surfaces since the alkali *ns* valence states overlap the conduction states of solids. Alkali adsorption is of great practical importance because of technological benefits such as enhanced catalytic activity and increased oxidation rates, which are both related to the charge transfer that occurs upon adsorption [1,2].

The most direct way to probe charge exchange is to investigate electron transfer during the scattering of low energy particles [3]. Such experiments indicate how charge transfer depends on the distance of an atom from the surface, and thus provide fundamental information concerning adsorption. Numerous experimental and theoretical studies have investigated charge transfer during the scattering of alkalis from metal surfaces [3–5]. Despite the importance of semiconductor materials, however, only a few have involved the charge transfer between alkalis and semiconductor surfaces [6–8]. In addition, no previous work has directly addressed clean semiconductor surfaces. This Letter investigates charge exchange between Li ions and clean Si surfaces. Hydrogen and cesium adsorbates are used to elucidate the role of surface states.

For alkali ion-metal collisions, the dominant electron exchange mechanism is resonant charge transfer (RCT) [3]. When an alkali is near the surface, the ionization level shifts and broadens so that it overlaps the Fermi level, which enables electrons to resonantly tunnel between the ion and the solid. The original RCT model ignored the details of the surface electronic structure and implied that the only relevant parameter is the surface work function. Subsequent experimental [9] and theoretical [10] investigations showed that what is actually probed is the local potential directly above the scattering site.

For semiconductors and insulators, the electronic structure is dominated by the band gap, and the density of bulk states near the gap is low. In addition, shifting and broadening of the ionization level due to the image charge, which is a critical part of RCT with metal surfaces, is expected to be weaker. Thus, it is unclear whether RCT will dominate neutralization for alkali particles scattering from semiconductors.

Clean Si has surface states, however, that can provide electrons for charge transfer. Charge transfer from surface states was previously proposed to explain negative ion formation in collisions of hydrogen and oxygen ions with Si(111) [11,12], although the process is nonresonant because of a relatively big energy difference between the anion level and the surface state. Souda *et al.* investigated the positive ionization of hydrogen from clean and passivated Si(111) surfaces, and reported a correlation between the scattered H^+ yields and the hydrogen coverage [13]. The charge transfer model they presented is that the incoming H ions first neutralize via an Auger process, then reionize during the violent collision, and finally couple with the dangling bonds along the exit trajectory. In this case, the charge transfer between the primary ion and the Si dangling bond is also not a resonant process.

We report two sets of experiments that are the first to directly illustrate how, and to what extent, RCT is influenced by the dangling bonds of a clean semiconductor surface. (1) When the dangling bonds are removed by hydrogen adsorption, the ion neutralization decreases. This provides direct evidence of the role of the dangling bonds. (2) Differences in the surface local electrostatic potential (LEP) between Si and Cs impurity sites cannot be discerned from ion scattering because the neighboring dangling bonds extend above the surface and screen the potential beyond the local surface site.

Time-of-flight (TOF) spectra were collected in an ultrahigh vacuum chamber, as is described in Ref. [9]. The 4.0 keV $^7Li^+$ beam had an energy spread of $<0.2\%$. The beam was deflected across a 1.0 mm^2 aperture to produce 40 ns pulses at a rate of 80 kHz. The beam was incident normal to the surface, and the scattering angle was 150°. The scattered ions and neutrals were detected by a microchannel-plate array after traveling through an

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electrically isolated flight tube. The total path length was 1.34 m. "Total yield" spectra were collected with the flight tube held at ground, while "neutrals only" spectra were collected by placing +1500 V on the tube to deflect scattered ions.

The Si surfaces were cleaned by standard methods. The overlayer symmetries were verified with low-energy electron diffraction, and the cleanliness was checked with x-ray photoelectron spectroscopy. The surfaces were reacted with atomic H by backfilling the chamber with H_2 in the presence of a hot tungsten filament located ~4 cm from the surface [14]. The exposures are based on the total pressure of H_2, and are reported in langmuirs (1 L = 10^{-6} Torr s). Thus, the atomic hydrogen exposures are much smaller than these values. Cs was deposited from a well-outgassed getter (SAES) with the surface at room temperature. Changes in the work function induced by H or Cs adsorption were measured by the energy shift of the secondary-electron cutoff generated by Mg $K\alpha$ x rays.

Representative total yield and neutrals only TOF spectra are shown in Fig. 1(a) for $^7Li^+$ backscattered from clean Si(111)-7 × 7. The single scattering peak (SSP) represents binary elastic scattering from a single surface atom, while the background arises from Li projectiles that have undergone multiple collisions. The SSP's are well resolved from the background in both spectra. TOF spectra collected from clean Si(100)-2 × 1 and H-covered Si surfaces (not shown) are qualitatively similar to those in Fig. 1(a).

Figure 2 shows the neutral fraction of the Si SSP and the surface work function as a function of hydrogen exposure. The neutral fractions of the singly scattered Li particles were determined by dividing the integrated area of the neutrals only SSP by that of the total yield SSP. The areas were calculated following the subtraction of a linear background (typical backgrounds are shown by dashed lines in Fig. 1). The neutral fractions in scattering from the clean surfaces are about 26%. As hydrogen is adsorbed, the work function decreases on both surfaces. A decrease of the work function is generally expected to lead to an increase of the neutralization probability, as has been commonly observed for metal substrates [3]. In contrast, however, the neutral fractions on both surfaces initially decrease. After a hydrogen exposure of a few hundred langmuirs, the neutral fractions begin to increase somewhat, but they never become larger than the clean surface values. Thus, there is no simple relationship between the H-coverage dependence of the neutral fraction and the surface work function, in contrast to H adsorption on metal surfaces [17].

At the initial stages of hydrogen adsorption on Si, H terminates the unsaturated surface dangling bonds [14,18] and eliminates the associated surface electronic states [19,20]. The neutral fraction of the scattered Li ions decreases considerably upon hydrogenation, which suggests that neutralization in scattering from the clean

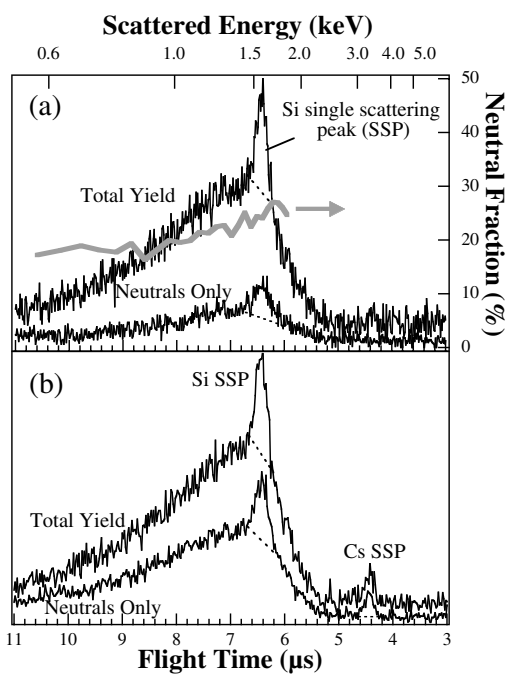

FIG. 1. TOF spectra of the total and neutral yields collected at a 150° scattering angle for normally incident 4.0 keV $^7Li^+$ scattered from (a) clean Si(111)-7 × 7, and (b) Cs-covered Si(111). The gray line in (a) shows the neutral fraction versus flight time.

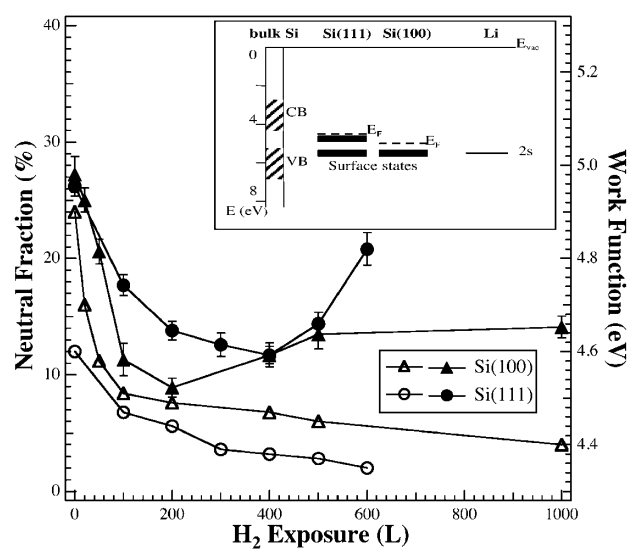

FIG. 2. Neutral fractions of scattered Li (solid symbols) and surface work function (open symbols) for Si(111) and Si(100) versus hydrogen exposure. The neutral fraction error analysis assumes that the uncertainty in the calculated SSP area equals the square root of the area. Inset is the energy level diagram of Li 2s, and the dominant surface states of Si(111)-7 × 7 [15] and Si(100)-2 × 1 [16]. The bulk Si conduction band (CB) and valence band (VB) are shown schematically at the left.

surfaces primarily involves the surface states. The inset of Fig. 2 shows the relative positions of the dangling bond surface states and the Li ionization (2*s*) level. The 2*s* level overlaps surface states for both Si(111) and Si(100), even without level shifting. RCT can therefore occur both from and to the partially filled surface dangling bond states. In the absence of surface states, the electrons available for exchange with the exiting Li must come from the valence band. Since the density of bulk states is low near the valence band maximum, the neutral fraction from the H-terminated surface is small. Thus, for alkali collisions with clean Si surfaces, RCT does occur because of the degeneracy of the surface states and the Li ionization level.

Similar neutral fractions are also found for single and multiple scattering from the clean surfaces. This is shown by the gray line in Fig. 1(a), which gives the neutral fraction as a function of flight time. In addition, for a given final energy, the neutral fraction of Li scattered from Si(111) is independent of the exit angle [17]. These results show that neutralization is largely independent of the site on the surface from which Li is emitted. This is particularly surprising for Si(111)-7 $\times$ 7, as there are only nineteen dangling bond sites per unit cell. Thus, although the dangling bonds are localized states, their influence extends over a large fraction of the surface.

The behavior on the hydrogen-terminated surfaces is similar to what has been reported for alkali ion scattering from insulator surfaces [21,22]. Insulators have a broad band gap and the density of surface states within the gap is negligible. As a result, little charge transfer occurs and the alkali projectiles exit the surface predominantly as ions [21]. This same effect is observed here when the Si is covered with hydrogen; i.e., the neutral fractions become very small.

When the hydrogen exposure is increased above what is needed to simply attach H to each dangling bond, Si-Si bond breaking occurs and the surface order is disrupted [14,23]. As the reaction proceeds, more Si-H bonds are generated forming higher hydrides, and more Si-Si bonds are broken. A consequence is the generation of "new" unpaired electrons, i.e., dangling bonds. Such states lead to a higher probability of electron exchange with the scattered Li, which may explain the slight increases in neutral fraction at larger H exposures. This effect appears to be greater for Si(111) than for Si(100), which is consistent with the fact that relatively more higher hydrides, and presumably more new dangling bond states, are formed on this surface [14].

Another major difference in ion scattering from Si and metal surfaces is in the ability of neutral fraction measurements to distinguish between sites with differing LEP's. We have previously investigated charge exchange for $^7Li^+$ scattering from cesiated Al(100), Ni(100), and Si(111) surfaces [8,9]. For Al and Ni, there is a clear difference in the neutral fractions collected from adsorbate and substrate sites. In contrast, for Cs/Si(111), the neutral fractions are nearly equal for the Cs and Si SSP's over the entire coverage range. Cs atoms are known to form ionic bonds to Si at low coverage [24,25], which means that the LEP at the Cs sites must be lower than that of the surrounding Si. Thus, it appears that Li ion scattering from Si is insensitive to variations in the LEP.

To investigate whether the surface dangling bonds are responsible for the inability of ion scattering to discern local effects for Cs/Si, the neutralization probabilities of $^7Li^+$ backscattered from cesiated Si surfaces were measured with and without hydrogen coadsorption. Typical TOF spectra of $^7Li^+$ backscattered from Cs-covered Si(111) are shown in Fig. 1(b). In all the spectra collected, the Si SSP's and Cs SSP's are well separated so that the neutral fractions can be independently monitored.

Figure 3 displays the neutral fractions of $^7Li^+$ scattered from clean, cesiated, and H/Cs-coadsorbed Si. To ensure that the surface potential is inhomogeneous, the Cs coverages were kept below 20% of saturation by monitoring both the work function and the intensity of the Cs SSP's in the TOF spectra. When Cs is deposited onto Si(111), the work function decreases and the Si SSP neutral fraction increases. The neutral fraction for $^7Li^+$ scattered from the Cs sites has a similar value as from Si, which is consistent with the previous work [8]. After atomic hydrogen is adsorbed, however, the neutral fractions diverge; i.e., the Cs SSP neutral fraction increases while that of Si decreases. For cesiated Si(100) in the absence of hydrogen, the neutral fractions for the Si and Cs SSP's are slightly different, but subsequent hydrogen adsorption greatly

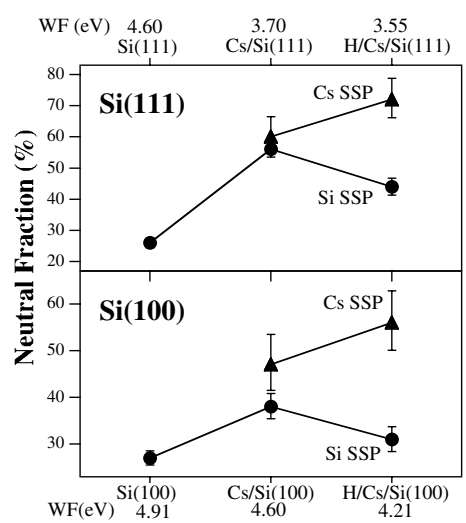

FIG. 3. Neutral fractions for 4.0 keV $^7Li^+$ scattered from clean, cesiated, and hydrogen-covered and cesiated Si(111) and Si(100). The neutral fractions for $^7Li^+$ singly scattered from Si and Cs sites are shown by ● and ▲, respectively. The corresponding work function (WF) values are shown at the top for Si(111) and at the bottom for Si(100).

magnifies the difference. These results suggest that, even in the presence of Cs adsorbates, the neutralization process is greatly influenced by the dangling bond states.

At the early stage of Cs adsorption on Si(111), Cs atoms react with the Si adatoms, but not with the rest atoms [26,27]. Thus, although the adatom dangling bonds are partially passivated, coupling between the Li and the rest atom dangling bonds can still occur. Since these highly active dangling bonds extend into the vacuum and are nearly perpendicular to the surface, the Li projectiles preferably interact with them as they leave the surface. As a result, the local effect of Cs adsorbates on the surface potential is washed out. When hydrogen is adsorbed onto Cs/Si(111), however, the hydrogen atoms tie up the remaining dangling bonds, which enables the ion neutral fractions to be sensitive to the LEP.

On Si(100), Cs initially adsorbs between neighboring dimer rows [28]. The Cs atoms may be large enough to also interact with the dangling bonds of neighboring dimers along the same row, or the dimers along the next row [28]. Therefore, Cs adsorbates on Si(100) may interact more strongly with the dangling bonds than on Si(111), which explains why the Si and Cs neutral fractions have slightly different values even in the absence of hydrogen. Subsequent hydrogen adsorption on Cs/Si saturates the remaining dangling bonds, which limits their influence so that the neutral fractions diverge further.

In summary, charge transfer in $^7Li^+$ scattering from clean Si surfaces involves RCT between the Li 2*s* level and the Si dangling bonds. Hydrogen adsorption decreases the neutralization because it ties up the dangling bonds. The neutral fractions in $^7Li^+$ scattering from Cs/Si are also determined primarily by the dangling bond states, so that the surface LEP cannot be directly probed. Hydrogen adsorption on Cs/Si ties up the dangling bonds, thereby revealing the local potentials. These results indicate that the charge transfer in alkali ion-semiconductor collisions is very sensitive to the surface electronic states.

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