LEED, AUGER AND PLASMON STUDIES OF NEGATIVE ELECTRON AFFINITY ON Si PRODUCED BY THE ADSORPTION OF Cs AND O

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We have made LEED, Auger, and Plasmon measurements to study how Cs and O adsorb onto the (100) surface of p-type degenerate Si to produce negative electron affinity (NEA). A key factor to producing NEA was found to be a highly ordered Si surface as reflected by very high quality $2 \times 2$ LEED patterns. When NEA is produced, both the adsorbed Cs and O give the same LEED pattern as the original Si surface, but with a general enhancement of the half-order spot intensity. The adsorption of both Cs and O is strongly self-limiting, apparently controlled by the number of available appropriate sites on the surface. If Cs and O adsorb amorphously, NEA is not achieved. The thermal desorption of Cs occurs over a fairly broad temperature range centered at about 550°C. After Cs desorbs, the remaining O reverts spontaneously from an ordered layer to an amorphous layer, and then desorbs at about 800°C with an activation energy of 3.3 eV.

Measurements of backscattered electron energy losses due to plasmons have shown that the Si surface plasmon is reduced in energy from 12.5 V to 7.0 V by the Cs-O layer. From this, an effective dielectric constant $\varepsilon = 5.3$ for this layer can be deduced which, in turn, enables us to characterize completely the Cs-O dipole layer.

The geometrical model described by Levine for the NEA surface is consistent with our experimental results.

1. Introduction

A condition of negative electron affinity at the surface of certain semiconductors can be achieved by suitable processing involving the adsorption of cesium and oxygen. This was first reported by Scheer and Van Laar\(^1\) while the current state of the art is described in a recent review article\(^2\). Negative electron affinity (hereafter called NEA) is said to exist when the vacuum level at the surface of the semiconductor is lower in energy than the bottom of the conduction band in the bulk. This is due to a combination of band bending at the surface and a lowering of the work function. The band bending results from surface states which pin the Fermi level at the surface, while the lowering of the work function is presumed to occur because of a surface dipole which is related to the adsorbed Cs-O layer.

NEA on Si was first reported by Martinelli\(^3\). As a result of this work and the work of others\(^4-6\), the important surface parameters related to NEA on degenerate p-type Si can be schematized as in fig. 1. The energy level scheme for the clean Si surface is shown in fig. 1a. In fig. 1b an amount of Cs has been adsorbed such that the work function is at a minimum and
Fig. 1. Energy levels at a silicon (100) surface relating to negative electron affinity. (a) Clean silicon; (b) After Cs adsorption; (c) After Cs and O adsorption resulting in NEA. $\Delta V$, the change in work function from (a) to (c), due to the Cs-O dipole, is 3.2 eV. The surface-state depiction is only schematic.

the photo-emission is at a maximum. The vacuum level has been lowered but is still above the conduction band edge. A new set of surface states has formed$^4$). Subsequent adsorption of the proper amount of O then lowers the vacuum level to below the conduction band edge resulting in NEA.

The atomic details of the way in which NEA is achieved have not been well understood. The cleanliness of the surface, the significance of the structural aspects of both semiconductor surface and adsorbate layers (or lack of it), the relative amounts and geometrical location of the O and Cs atoms, the binding energies of these atoms to the activated surface, have not been established. In this paper we report the principal results of a comprehensive study of NEA on Si, directed toward clarifying these matters. We have used low energy electron diffraction (LEED) to obtain structural information, Auger electron spectroscopy to monitor relative amounts of different atoms on the surface, and various surface treatments such as sputter-cleaning and annealing, to relate surface condition to activation state. We have measured thermal desorption of the adsorbate atoms to determine their binding energies. Finally, we have used the LEED electron optics for characteristic energy loss (plasmon) measurements from which we have derived some unique properties of the adsorbed layers$^7$). Our experimental results will be discussed within the framework of the geometrical model for the NEA surface proposed by Levine$^{23}$). Silicon was chosen for this study because of all the semiconductors for which NEA has been
reported it is the simplest*, and more is known about it and its surface than any other.

2. Experimental results

2.1. Apparatus

The work was performed in a stainless-steel bakeable, ultra-high vacuum system containing four-grid LEED-Auger optics8,13) which was obtained commercially. The pumping system was comprised of sorption roughing pumps and ion high-vacuum pumps. Titanium sublimation, and occasionally cryogenic panels, were used when increased pumping speeds were desired. Base pressures of 5 to \(10 \times 10^{-11}\) torr were obtainable, although during operation the pressure rose to working levels of 1 to \(5 \times 10^{-10}\) torr. Various operational stages were incorporated into the vacuum system and are shown schematically in fig. 2. In addition to the LEED-Auger optics there are a photoemission analyzer, a Kelvin probe for measuring work function, a sputtering stage using 400 V argon ions operating at an argon pressure of \(~10^{-4}\) torr, a cesium ion gun, a molecular Cs source9)**, and an electron bombardment heater. Several samples in the form of thin wafers were mounted in a specimen manipulator, which could be rotated to any of the appropriate positions. Oxygen was admitted to the system through a heated

* All other semiconductors for which NEA has been reported are compound semiconductors9).

** In this work, Cs from the molecular source was used throughout.

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Fig. 2. Schematic diagram of vacuum system containing experimental apparatus.
silver plug\textsuperscript{10}); argon (research grade) was admitted through a variable leak valve.

LEED patterns were recorded photographically from a phosphorescent screen at various stages in the surface treatments and activation procedures. Primary electron beam voltages up to several hundred volts were used, although we found that our most useful voltages were 85 V and 179 V. Auger spectra were recorded in the form of the derivative of the energy distribution $dN(E)/dE$ versus retarding voltage. The energy and current of the primary electron beam were typically 3 kV and 100 $\mu$A, respectively, except where otherwise stated. Electronic and other details of the LEED and Auger systems are essentially those of the type described in ref. 13.

One experimental problem may be worth noting. During the course of this work, indications of charge build-up on the repeller grids developed. One such indication was the appearance of a very steep slope in the base line\textsuperscript{11) of the Auger spectra at retarding voltages less than about 250 V which sometimes made the observation of small Auger peaks in this region very difficult. This problem was circumvented by biasing the sample and the first grid at $-300$ V with respect to ground, which had the effect of shifting the entire Auger spectrum 300 V to higher values of retarding voltage\textsuperscript{*}. The fact that a charge existed on the grids implied, of course, that a thin insulating layer had formed on the grids. It is believed that such layers were oxides of cesium and silicon, formed first by their deposition on the grids during activation and sputter-cleaning procedures, respectively, followed by exposure to oxygen when the system was opened.

2.2. CRYSTAL PREPARATION

The silicon crystals used in this work were obtained from Monsanto. They were melt-grown, boron doped to about 0.01 $\Omega$-cm, oriented and cut to the $\langle 100 \rangle$, $\langle 110 \rangle$, and $\langle 111 \rangle$ directions, and finally chemically-mechanically polished. A final cleaning procedure\textsuperscript{12) was performed\textsuperscript{+} immediately prior to mounting in the vacuum system. It consisted of a chemical etch followed by the growth of an oxide layer to a depth of about 4000 Å. The oxide and those contaminants which may have been left on the original surface were then stripped off by HF, washed in doubly distilled water, and spun-dried. Auger spectra taken of these surfaces before any sputter-cleaning or heating showed only trace amounts of carbon and oxygen.

2.3. ACTIVATION PROCEDURES

The procedures used to activate NEA surfaces are basically those evolved

\textsuperscript{*} I am indebted to C. T. Hollish for valuable discussion on these points.

\textsuperscript{+} Very kindly performed by J. Breece.
by Martinelli\textsuperscript{3}, with minor modifications. After the vacuum system was baked out, the wafers were heated at 1000°C for 5 min, sputter cleaned for 15 min, then annealed for about 30 min at 900 to 1000°C. If the Auger spectrum and the LEED pattern were satisfactory, cesium was deposited on the silicon until a maximum in the photoemission was reached and passed. At this point, the photoemission would slowly drift back toward its maximum value. The surface at this first photoemission maximum will be referred to as Si/Cs, and corresponds to fig. 1b. The degree of overshoot past the photoemission maximum is not crucial. Oxygen was then admitted to the system, and the photoemission continuously monitored until another maximum was reached several hundred times larger than the first one. The second maximum is much more sharply peaked than the first, but here too, if one overshoots, the photoemission will drift back toward the maximum. The surface at this second maximum will be referred to as Si/Cs/O, and corresponds to fig. 1c. The photoemissive efficiency corresponding to what we define as a "successful activation" is several hundred micro-amperes per lumen\textsuperscript{3}). Such high values are attained only from the fully activated Si/Cs/O surface. That such surfaces exhibit NEA is established by the fact that the low-energy threshold in photoemission yield curves has decreased to the point where it has become limited by the silicon bandgap\textsuperscript{3}).

2.4. LEED-AUGER MEASUREMENTS

2.4.1. Production of NEA surfaces

The important differences in the state of the silicon surface between successful and unsuccessful activation attempts were found to be structural as indicated by LEED. For both cases the Auger spectra of a clean Si surface were essentially the same, showing no traces of oxygen or carbon. There were visible only the silicon lines (including a completely resolved 35 V line)\textsuperscript{13}), the (dopant) boron line, and a line due to a trace arsenic impurity which did not appear to affect our results. A typical spectrum is shown in fig. 3.

The LEED patterns, however, indicate the following structural differences. The surface prior to an unsuccessful activation gave LEED patterns which had blurred or streaky spots or spots with spherical halos (not shown here), while the LEED patterns of surfaces prior to successful activations had more sharply defined and brighter spots with a darker background, indicative of less diffuse scattering. This indicates that the "successful" surfaces had a significantly higher degree of order in its structure than in the "unsuccessful" surfaces, although Auger spectra for both were the same. The correlation between an ordered surface and a successful activation was also conspicuous after activation. In fig. 4 we show data analogous to fig. 3, but for surfaces
after activation. Again, Auger spectra for successful and unsuccessful activations are practically the same showing similar amounts of cesium and oxygen*. However, the successful activation gives a well-defined LEED pattern, indicating the same basic structure in the Si/Cs/O surface as that of the clean silicon surface, although with different spot intensities; the Si/Cs/O surface for an unsuccessful activation appears to be amorphous.

* The adsorption of O actually increases somewhat the Cs Auger electron signal, as was found by King14). This is discussed later on in terms of increased backscattering of these electrons.
Fig. 4. Auger spectrum and LEED patterns (at 85 V) of Si (100) after (a) unsuccessful, and (b) successful activations to NEA.

The basic LEED pattern seen in figs. 3 and 4 is the $2 \times 2$ reported by earlier workers\cite{12,16}, but with spot intensities which vary with order and beam voltage in a nonregular way. Taking LEED patterns at 179 V where more unit cells of the pattern (higher order spots) are included, produce the same general behavior indicated in figs. 3 and 4: however, in this case another aspect of the activation process is observed which is related to the surface structure. Before activation, the LEED pattern generally has the integral order spots brightest and the half-order spots dimmest. After activation,
the half-order spots have grown brighter, while the integral order spots have grown dimmer.

In figs. 5a, 5b, and 5c, we show LEED patterns at 85 V during the process of formation of a Si/Cs/O surface. They show that the intermediate stage – a Si/Cs surface – has the basic structure of the clean silicon surface as well as the final Si/Cs/O stage. However, anticipating a later result, we note here that oxygen adsorbs with this structure only when cesium is adsorbed first.

The amount of cesium and oxygen adsorbed during activation appears to be limited. After some “proper” amount has been adsorbed, Auger spectra show no increase in either cesium or oxygen after as much as ten times the exposure to these adsorbates, nor is there any discernible change in the LEED pattern. There may temporarily be additional adsorption, but if there

![Image of LEED patterns](a) ![Image of LEED patterns](b) ![Image of LEED patterns](c)

Fig. 5. LEED patterns (at 85 V) corresponding to (a) clean Si<100>, (b) Si/Cs, and (c) Si/Cs/O surfaces. Although spot intensities vary somewhat, the basic structure of all three surfaces is the same.
is, it is so weakly bound that it desorbs very easily and quickly at room
temperature – witness the drift back to maximum photoemission after
overshoot described earlier. Similar overshoot behavior in work function
measurements has been observed 3).

If oxygen is adsorbed first and cesium is adsorbed second, a silicon surface
will not successfully activate. On clean silicon, oxygen has a sticking coeffi-
cient at least 100 times smaller than it has on cesiated silicon. When amounts
of oxygen and cesium (deposited sequentially) required for activation (as
measured by their Auger lines – see fig. 4) are adsorbed onto a clean silicon
surface, LEED patterns show that both oxygen and cesium adsorb as
amorphous layers.

2.4.2. The stability of the surfaces and observed defects

A sputter-cleaned and annealed silicon surface in a vacuum \(\sim 10^{-10}\) torr
will maintain its LEED pattern for several days. Even though minute traces
of carbon and oxygen become visible in Auger measurements after a day,
the LEED pattern seems to have suffered only little. Using a time-pressure
exposure, and the assumption that about 0.5 to 1 monolayer is required to
significantly degrade a LEED pattern, this suggests that the sticking coeffi-
cient for oxygen and carbon monoxide (the chief contaminants in the vacuum
system) is less than about 0.01. Nevertheless, even after an overnight period,
the Si/Cs/O surface must be recleaned in order to produce NEA. After the
cesium step in the activation procedure, the surface is stable for 1 to 2 hr.
Subsequent exposure to oxygen then completes the activation as described in
section 2.3. The activated Si/Cs/O surface, however, degrades in several
hours. After overnight the photoemissive efficiency is less by at least an order
to magnitude. The LEED pattern is only slightly dimmer, but Auger
spectra show that along with the trace contamination of carbon mentioned
earlier, the oxygen has increased by 20 to 30\%\). As indicated earlier, this is
more than enough to seriously lower the activation state*.

Two specific types of defects were observed in our silicon LEED patterns –
streaked spots with the streaks along the edges of the squares formed by the
spots, and spots with spherical halos around them which we interpret as
merely large spots produced along with the regular small spot. Both these
defect types have been associated with domains on the surface which are
smaller than a certain critical coherence diameter\(^{17}\)). The fact that proper
annealing can eliminate these defects from the LEED patterns seems con-
sistent with domain size effects.

* It is certainly possible that the behavior described here may be somewhat different in a
different vacuum chamber.
2.4.3. Other primary surfaces

Attempts to activate the (111) and (110) surfaces to NEA with procedures similar to those described above were unsuccessful, as were attempts by other workers. The photoemissive efficiencies were increased, but this was due to the lowering of the work function due to cesium coverage as reported by others. We have observed, as have others, that on both the (111) and (110) surfaces, adsorption of cesium and/or oxygen destroys the well-defined LEED pattern of the clean surface, introduces no new pattern of its own, and thus adsorbs in an amorphous layer.

2.5. Thermal desorption

In fig. 6 we show the thermal desorption of cesium and oxygen from a Si/Cs surface and from a Si/Cs/O surface. The relative amounts of cesium and oxygen remaining on the surface at room temperature, as indicated by their Auger line intensities, are plotted versus the temperature to which the surfaces were heated just prior to the measurement. The heating time was 1 min, after noting that the results were essentially the same within experimental error for times from 1 to 3 min. Cesium desorbs from the Si/Cs surface over a fairly broad temperature range centered at about 450°C. The cesium desorption from the Si/Cs/O surface has a similar behavior except that the curve shifts about 100°C to higher temperatures. At about 800°C
Fig. 7. LEED patterns (at 85 V) of Si ⟨100⟩ at various desorption stages. Note lack of order in O layer as Cs desorbs (T = 550°C). (a) Clean LEED pattern; (b) activated, not heated; (c) 300°C; (d) 450°C; (e) 550°C; (f) 900°C, 5 min.
the oxygen desorbs over a narrow temperature range and, in an Arrhenius plot, yields an activation energy of 3.3 eV.

Room temperature LEED patterns of the Si/Cs/O surface were taken at various stages during the desorption experiments and are shown in fig. 7. At 300°C, even though there is no discernible change in either LEED pattern or Auger spectrum, the activation (as measured by photoemissive efficiency) has dropped by more than an order of magnitude. This is consistent with our earlier finding that it takes very little departure from the correct amount of oxygen on the surface to seriously affect the activation level. Note that as cesium desorbs the characteristic LEED pattern disappears. When only oxygen is left on the surface, the pattern has reverted to one characteristic of an amorphous layer – which is the LEED pattern observed when only oxygen is adsorbed on silicon (100) without cesium.

At 900°C, after both cesium and oxygen have desorbed, the LEED pattern of a well-ordered, clean silicon surface re-appears.

2.6. SURFACE PLASMON MEASUREMENTS

The purpose of these measurements was to help characterize the Si/Cs/O surface by noting the changes, if any, in the silicon plasmon spectrum. The same LEED optics used for Auger spectroscopy was used for plasmon measurements by choosing an appropriate primary beam energy, and examining the energy distribution of the backscattered electrons in the region just below the elastic peak. For a general survey of plasmons, the reader is referred to reviews by Raether\textsuperscript{19} and Pines\textsuperscript{20}.

In fig. 8 we show two characteristic loss curves of clean silicon for primary beam energies of 40 V and 100 V. In the 100 V curve we can clearly see one and two bulk plasmon losses of about 17.5 V each, and one surface plasmon loss of about 12.5 V. The energy of the latter is about \( \frac{1}{\sqrt{2}} \) times that of the former, in good agreement with theoretical expectations\textsuperscript{21}.

A series of characteristic loss curves were then taken at constant primary beam current (2.5 µA) and energy (40 V), from surfaces of (a) Si, (b) Si/Cs, (c) Si/Cs/O, and (d) silicon which has only oxygen left on the surface after desorbing cesium. In (a), only one bulk plasmon and one normal silicon surface plasmon are seen. With the adsorption of cesium (b) (which incidentally prevents beam penetration to some degree, thereby emphasizing surface plasmon excitations) the silicon surface plasmon changes to 7 V. In case (c) after oxygen adsorption, the 7 V plasmon structure becomes better defined, while all trace of the bulk plasmon has disappeared. After the desorption of cesium at 700°C, the 7 V plasmon disappears, and even though the oxygen remains (see previous section), the plasmon spectrum looks essentially like that of clean silicon. These plasmon results are the same when cesium and
oxygen are adsorbed on (100) in such a way as to produce no NEA, and when cesium and oxygen are adsorbed on (111) and (110) surfaces of silicon.

Our interpretation of these results is simply that when the Cs or Cs-O layer is adsorbed, the silicon surface is no longer bounded by a medium with unity dielectric constant but rather by some effective dielectric constant $\varepsilon$. Accordingly, the energy of the silicon surface plasmon will be that of the bulk plasmon divided by $\sqrt{1 + \varepsilon}$ rather than by $\sqrt{2}$. The surface plasmon has been 'relaxed' from 12.5 V to 7 V by an adsorbed Cs or Cs-O layer with an effective dielectric constant of 5.3.

### 3. Discussion

The most salient feature of the adsorption of Cs and O on Si (100) and the subsequent production of negative electron affinity, is its correlation with a high degree of order of the pre- and post-activated surface. A chemically clean Si surface, for which sputtering and annealing are required, is a "necessary" but not a "sufficient" condition for activation to NEA. The clean surface must, in addition, exhibit high quality LEED patterns (fig. 3). If the order in the Si surface is not sufficient, the Cs and O adsorb in an amorphous layer, and NEA is not achieved (fig. 4): If the order is sufficient, the Cs and the O adsorb as a highly ordered surface layer, both having a
unique unit mesh dimension of twice the original unreconstructed Si surface (fig. 5), and NEA is achieved.

The geometrical model for the Si/Cs/O surface in terms of which our results will be discussed is described in detail by Levine\textsuperscript{23}). It stems from the model for the clean, reconstructed Si (100) surface suggested by Schlier and Farnsworth\textsuperscript{16}) to explain the generally observed $2 \times 2$ LEED pattern. Their picture has adjacent rows of Si atoms pulling together as their dangling bonds (2 per atom) join and saturate, giving a repeating unit cell of twice the dimension of that of the unreconstructed Si surface, as illustrated schematically in fig. 9b. This produces the $(\frac{1}{2}, 0)$ spots, while similar reconstructions in the vertical direction give $(0, \frac{1}{2})$ spots. One consequence of rows of adjacent Si atoms pulling together is the opening up of unusually large hexagonal caves or pores (dashed line, fig. 9b), which have the same repeating unit cell dimension as the row pattern just described and as outlined by the rectangle in fig. 9b. The geometrical model for the Si/Cs/O NEA surface\textsuperscript{23}) is one in which the Cs sits atop the close rows of Si atoms, the O occupies the caves below the original surface of the Si, and the dipole layer required to lower the work function to produce NEA is formed by the transfer of charge from Cs to O. This geometrical model is shown schematically in fig. 10.

The model fulfills the prime requirement that it explain the LEED data. The Cs and O both occupy sites which give the same $2 \times 2$ LEED patterns as the clean reconstructed Si surface: and since Cs may be expected to be

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig9.png}
\caption{Model of (100) Si surface after Schlier and Farnsworth. The close rows of atoms and the hexagonal "caves" both give rise to unit cells with twice the dimension of that of the unreconstructed surface as shown, and produce the half-order LEED spots. What is shown would produce a $2 \times 1$ LEED pattern. The presence of domains with equally probable structures rotated $90^\circ$ would then produce the $2 \times 2$ LEED structure.}
\end{figure}
Fig. 10. The geometrical model for the Cs and O layer suggested by Levine. The unit cells defined by both the Cs and O atoms have the same dimension as that seen in fig. 9b for the reconstructed Si surface.

a more effective electron scatterer than Si, the half-order spots ought, in general, be more intense.

In addition, the sensitivity of the structural quality of the adsorbed layers to that of the Si surface can be readily understood. Any non-regularity, impurity, or point defect could produce extensive regions of strain and distortion on the Si surface and thus interfere with the adsorption of highly ordered layers of Cs and O. Note also that almost all other possible sites for Cs seem unlikely by virtue of the fact that such sites have randomly equal alternatives which would produce a non-unique unit mesh dimension, and such a situation would not produce a sharp spot pattern.

The model is consistent with several other of our experimental findings of a geometrical nature. Of the three primary crystallographic surfaces, NEA can be produced only on the (100) (section 2.4.3): and indeed neither the (110) nor the (111) surface offers pores or caves of such size as to accept and hold O as it can on the (100). In addition, it has been found that for successful activations, Cs must be adsorbed first, followed by O (section 2.4.1). This can be explained by the fact that O adsorbs onto clean Si amorphously: thus, if we tried to activate the Si surface by adsorbing O before Cs, we would produce non-ordered layers which our results have shown do not produce NEA.

The model for the Si/Cs/O surface also furnishes a ready explanation for the self-limitation observed in the Cs and O adsorption process, for it constrains the Cs and O to adsorb only on specific sites which have a fixed

* However, not all half-order spots, because of contributions from some subsurface scattering.
areal density. When these sites are filled, further adsorption should stop or decrease sharply, and the sticking coefficient should drop drastically as we have observed (section 2.4.1). Weber and Peria) have measured the amount of adsorbed Cs corresponding to a minimum in the work function and found it to be very close to a half monolayer, which is of course precisely the areal density of the available sites for Cs in the atomic model (fig. 10).

We now discuss some of our experiments in the light of the electronic aspects of the model. Two observations in our desorption experiments suggest that Cs and O are electronically bound together – apart from the obvious fact that they are supposed to form the ends of the surface dipole layer. First, more energy is required to desorb Cs from a Si/Cs/O surface than from a Si/Cs surface (see fig. 6). Analysis of these data in terms of an activation energy linearly dependent on coverage23,24), indicate that at zero Cs coverage, this energy is 2.88 eV for the Si/Cs/O surface, and 2.77 eV for the Si/Cs surface*. Secondly, note in fig. 8 that when Cs desorbs from a Si/Cs/O surface, leaving only O, the LEED pattern disappears, i.e., O has reverted spontaneously to an amorphous layer. We conclude from this that the Cs is directly responsible for the ordered structure of the O, presumably by making sites involving the uppermost layer of Si atoms unavailable to the O. Clearly, the presence of the surface “caves” without the presence of the Cs is not sufficient to produce an ordered O layer. It is worth mentioning that the change from order to disorder requires some motion of the O on the Si surface.

In section 2.4.1, we mentioned that the adsorption of O onto a Si/Cs surface increased the magnitude of the Cs Auger lines. It had been suggested 25) that this might be due to the fact that the O layer, filling voids underneath the Cs layer as in fig. 10, increases the elastic backscattering of those Cs Auger electrons directed initially into the bulk of the Si crystal. This seems to be directly substantiated by an experiment in which an electron beam of the same energy as the Cs Auger electrons (e.g., 48 V) was directed first onto a Si/Cs surface and then onto a Si/Cs/O surface. The magnitude of the elastic peak in the energy spectrum of the reflected electrons was about 40% greater from the latter surface than from the former.

We will close our discussion by describing the role played by the plasmon measurements in elucidating some of the electronic properties of the dipole produced by the Cs–O layer. These plasmon measurements make two principal contributions. First, they help to characterize the Cs–O layer by a property of that layer, i.e., the energy of the Si surface plasmon is “relaxed”

* Such coverage-dependent desorption also accounts qualitatively for the rapid initial desorption rate followed by the much slower later desorption rate observed in our experiments (see section 2.5).
from 12.5 V to 7.0 V when Cs and O are adsorbed according to the model. Second, and more importantly, they furnish us with an effective dielectric constant for completing the electronic description of the “Cs–O” dipole. The magnitude of this dipole, given by $\Delta V$ in fig. 1, can be expressed either as $\Delta V = 4\pi \sigma f q L$ or $\Delta V = 4\pi \sigma q L / \varepsilon$ where $\sigma$ is the areal density of the dipole ($3.4 \times 10^{14}$ /cm$^2$, i.e., the half monolayer of Cs and O shown in fig. 12), $f$ is the fraction of unit charge $q$ transferred or shifted over the distance $L$, and $\varepsilon$ is the effective dielectric constant. Heretofore, in problems of this type, only the product $fqL$ could be calculated: independent measures of $fq$ or of $L$ were very difficult. With a knowledge of an effective $\varepsilon$, however, values for $L$ and $fq$ can be readily calculated. In the case of the Si/Cs/O layer discussed here, $L = 2.8$ Å, and $fq = 0.19$ unit charge. A value for $L$ can also be readily determined solely from the geometrical model in terms of internuclear distances between atoms whose positions are known. This results in an $L$ value of 2.9 Å, in good agreement with the electronically calculated value.

Note that the effective dielectric constant is practically the same for the “Cs–O” dipole (on the Si/Cs/O surface) as for the “Cs-surface state” dipole (on the Si/Cs surface) even though the strength of the “Cs–O” dipole is larger, i.e., lowers the work function a bit more, see fig. 1. This is due to the fact that the “Cs–O” dipole is longer since the oxygen atoms are submerged below the Si surface. This increased length properly accounts for the difference in dipole strength even though the effective dielectric constant is the same.

4. Summary and Conclusions

The production of negative electron affinity on the Si (100) surface due to the adsorption of Cs and O requires a highly ordered, chemically clean surface. Furthermore, the Cs and O must adsorb in an ordered layer: if they adsorb amorphously, due for example to an insufficiently prepared Si surface, NEA is not achieved.

The structure of both the Cs and O layers is the same as the reconstructed clean Si surface, although the adsorption of O in an ordered layer is crucially dependent on the previous adsorption of Cs in an ordered layer.

The adsorption of Cs and O has a self-regulating factor which sharply limits the final amounts of Cs and O adsorbed.

The thermal desorption of Cs from a Cs–O layer requires more thermal energy than from a Cs-only layer. When Cs desorbs from an ordered Cs–O layer, the O loses its order and becomes amorphous.

* As discussed in detail in ref. 23.
The Cs–O layer strongly affects the surface plasmon energy of clean Si, changing it from 12.5 V to 7 V. From this, an effective dielectric constant for the Cs–O layer can be calculated to be $\varepsilon = 5.3$, which then leads to a complete characterization of the dipole layer.

The geometrical model for the NEA surface proposed by Levine is consistent with all our experimental results. Specifically, it can account for the LEED behavior, why only the (100) surface activates to NEA, the importance of a highly ordered Si surface, the self-limiting factor found in the Cs and O adsorption processes, and the geometrical aspects of the Cs–O dipole layer.

Acknowledgements

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References

6) R. U. Martinelli, to be published.
11) G. Bohn, private communication.
12) A. M. Goodman and J. M. Breece, to be published.
25) This suggestion was made by A. Rothwarf.
Discussion

C. CAROLI (Laboratoire de Physique de Solides de l'ENS, Paris)
I have not really understood what is that dielectric constant of the adsorbate layer you have been speaking about, since you are dealing with only a monolayer of the adsorbate.

B. GOLDSTEIN
Conceptually, it is certainly not the classical Gaussian pillbox dielectric constant which, I agree, requires more bulk than one monolayer. But even this one monolayer has a polarizable electron distribution within the cesium-oxygen complex. I would suggest that it is in terms of this polarizability, P, that the effective dielectric constant of which I spoke may be conceptualized.

H. P. BONZEL (Ford Motor Co., Dearborn, Mich.)
I would like to point out that energy loss spectra for very low primary beam energies (< 80 eV) were recently reported by Steinrisser and Sickafus [Phys. Rev. Letters 27 (1971) 992; J. Vacuum Science Technol. 9 (1972) 603] for Ni(110) surfaces. These authors gave a completely different interpretation of observed loss peaks where the main emphasis was on interband transitions involving molecular orbital excitations for adsorbed nitrogen and sulfur.

B. GOLDSTEIN
I think there are several reasons why these losses I have observed are plasmon losses rather than interband transitions. First, even though I have only shown curves for primary beam energies of 40 V, exactly the same losses, and no others, are observable for primary beam energies ranging up to several hundred volts. I would think that if optical interband transitions are involved, I should see some other such transitions appearing as my primary beam voltage increased. Secondly, if a half monolayer of cesium introduced interband transitions of 7 V, I should think that I would still see the original 12.5 V silicon surface plasmon. However, this is not the case: there is no trace of the 12.5 V transition in my curves with a half monolayer of cesium. And, third, the losses, if interpreted as plasmon losses, have an energy which leads to dipole properties which are in excellent agreement with those properties as deduced by other in dependent means as discussed in the paper.