

## Negative Electron Affinity and Low Work Function Surface: Cesium on Oxygenated Diamond (100)

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Building on analogies with low work function metal surfaces, an oxygenated C(100) surface cesiated at the half-monolayer level has been studied with self-consistent local-density-based methods. Cesium of the surface is found to shift the 2.45 eV positive electron affinity oxygenated surface to a surface with the bulk diamond conduction band 0.85 eV above the vacuum level, in effect a 0.85 eV negative electron affinity (NEA). The resulting surface is in fact metallic due to Cs-O-C surface states and thereby also provides a low work function  $\Phi = 1.25$  eV. The combination of NEA bulk material with metallic low- $\Phi$  surface promotes noncharging electron emission that makes it promising for novel diamond-based optoelectronic devices.

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The electron affinity (EA)  $A$  of a collection of atoms, say a solid, is the difference in energy between the neutral solid plus an electron at infinity, and the electron absorbed onto, or into, the solid. Normally  $A > 0$ : An extra electron will stick. If (taking a one-electron picture for definiteness) the solid has no unoccupied conduction band (CB) states below the vacuum level, then it has a negative EA (NEA), and an electron introduced or excited into the CB will be emitted from the surface because it can gain energy by dropping to the vacuum level.

NEA surfaces of semiconductors are attracting renewed interest because they impact a broad class of important optoelectronic devices including field emitters and photoemitters. When band gap radiation excites electron-hole pairs near the surface, the electron can be emitted spontaneously from a NEA surface, resulting in a directed electron beam that is readily controlled with applied fields. Diamond surfaces have been discussed in this context since the report of NEA behavior of the C(111) surface by Himpsel *et al.* [1] that was attributed to H coverage of the surface [2]. Experimentally, NEA behavior means simply that electrons at the bulk CB minimum are emitted from the surface. Wide gap semiconductors seem like natural candidates for NEA surfaces, since their wide band gap is more likely to put the conduction band minimum near or above the vacuum level. More often, NEA surfaces result from organic solids or from semiconductor surfaces covered by molecules or metals [3].

Recently H-saturated diamond surfaces have been studied more thoroughly, and the C(100) surface annealed above 1000 °C was found to have a NEA signature [4]. This result was attributed, based on electronic structure calculations, to a monohydride C(100) surface [4] and the predicted value was  $A = -2.2$  eV. Field emission characteristics of diamond films have been measured recently and remain the topic of some controversy [5,6]. Since cesium and cesiated metal surfaces form the basis

of many cold cathodes, it is a rather obvious question to ask whether Cs will promote NEA effects on diamond surfaces, and whether diamond films can provide the basis for NEA devices.

Achievement of NEA semiconductor surfaces is analogous to the treatment of metal surfaces to produce low work functions for application as cold cathodes. Monolayer coverage of transition metal (TM) surfaces (e.g., W, Re) by alkali metals, especially Cs, has been studied rather thoroughly via electronic structure calculations (see, e.g., [7]), with the work function lowering of a few eV being the result of dipole formation resulting from electron rearrangement within the surface region. In applications, cold cathodes use the much more stable BaO-saturated TM surfaces, which have also been studied theoretically [8] and interpreted in terms of dissociated Ba and O species on the surface. Recently Geis reported [9] remarkable stability of cesiated diamond surfaces, if the surface was first oxygenated. The resulting surface was unreactive and displayed promising field emission characteristics.

This Letter provides a theoretical prediction of a cesiated oxygen-stabilized diamond surface that should have excellent field emission characteristics. The C(100) surface was chosen for this study, because it is the dominant growth surface in the chemical vapor deposition (CVD) of diamond films on a variety of substrates and thus is readily available for use. For monolayer coverage by oxygen, which allows a C-O-C (ether) bonding configuration, an insulating surface with a conventional positive EA results. Addition of one-half monolayer of Cs is found to produce a shift of the surface dipole by 3.3 eV, resulting in an effective NEA  $A = -0.85$  eV for this surface.

The local-density-based calculations were done with a generalization of a full potential, all electron, linearized augmented plane wave code [10] which has additional local orbitals [11] to allow all valence and semicore states to be treated self-consistently within a single energy window. The Cs  $5p$  semicore states, which are known to

contribute to the bonding and to the dipole formation at TM surfaces, are thereby included fully self-consistently. The underlying structure is a ten layer slab of C atoms in the diamond structure, and for computational efficiency inversion symmetry was retained in all geometries. Oxygen was added at the bridge site. For this surface all atomic positions were relaxed beginning with the C-O distance obtained by Whitten *et al.* [12] from cluster calculations. This structure provided the substrate to which Cs was added (ratio Cs:O = 1:2). At the height of the Cs layer given in Table I the force on the Cs atoms was very small, so no further relaxation was necessary. The basis set size was  $\sim 3750$ , with diagonalization done mostly by iterative techniques.

Because of the large Cs ion and the small lattice constant of diamond, even this half monolayer of Cs puts the Cs ions rather close together. The Cs-Cs separation is  $0.2 \text{ \AA}$  greater than twice the Cs ionic radius ( $r_{\text{ion}} = 1.69 \text{ \AA}$ ) and may be realizable. Rb ( $r_{\text{ion}} = 1.48 \text{ \AA}$ ) would be an alternative choice. The large ionic size is expected to be important, however, because (i) it contributes to the low electronegativity (encouraging charge transfer and dipole formation), and (ii) it keeps the Cs-O separation larger than would be the case for small alkalis, so a given amount of charge transfer leads to a larger dipole. This surface, in which Cs is fourfold coordinated with O atoms and each O is bonded to two C atoms and twofold coordinated to Cs, is visible in Fig. 1.

In a film calculation it is impossible to obtain bulk band edges precisely from band states alone, but the identification can be done accurately [13] using the interior C  $1s$  states together with reference calculations carried out concurrently for the bulk. The diamond valence band (VB) maximum is found to lie  $7.95 \text{ eV}$  below the vacuum level, and adding the experimental band gap of  $5.5 \text{ eV}$  puts the bulk CB minimum  $2.45 \text{ eV}$  below the vacuum level. The true EA of this surface depends on the position of the unoccupied O-C surface bands, whose precise position

TABLE I. Layer positions ( $z$ ) for the Cs( $2 \times 2$ ) monolayer on C(100):O, in terms of the lattice constant  $a = 3.567 \text{ \AA}$ .  $\delta z$  denotes the layer relaxation before addition of Cs; the number for O in parentheses represents the O layer position with respect to the next C layer in the diamond structure. C1 denotes the innermost layer of the ten layer diamond slab, while C5 is the outermost layer. In the  $x$ - $y$  plane, Cs is centered between four O atoms.

	$z/a$	$z(\text{\AA})$	$\delta z(\text{\AA})$
C1	0.1250	0.446	0.0
C2	0.3725	1.329	-0.009
C3	0.6187	2.207	-0.022
C4	0.8688	3.099	-0.022
C5	1.1094	3.957	-0.111
O	1.3312	4.748	(-0.156)
Cs	2.0407	7.279	...

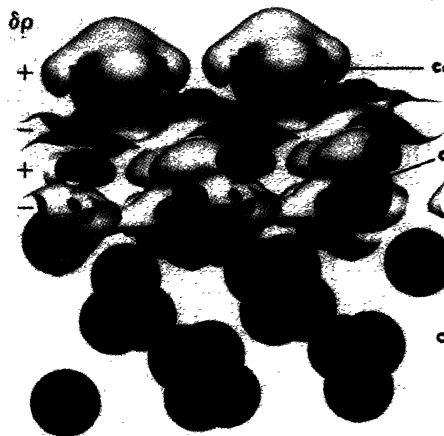


FIG. 1. The spheres indicate the atomic positions (as noted) for half of the slab with a  $c(2 \times 2)$  overlayer of Cs on the C(100):O surface. The surfaces represent constant values ( $\pm 0.0013 \text{ a.u.}$ ) of the difference of charge densities  $\delta\rho$ : Cs( $2 \times 2$ ) layer on oxygenated C(100), minus the superposition of oxygenated C(100) and an isolated Cs monolayer. Plus and minus signs indicate the sign of  $\delta\rho$  at that height.

would require a surface self-energy calculation (we return to this point below).

Adding the Cs overlayer shifts the diamond VB maximum to  $4.65 \text{ eV}$  below the vacuum level, and adding the experimental band gap leads to a bulk CB minimum  $0.85 \text{ eV}$  above the Fermi level. The cesiated surface is metallic, with the Fermi level  $E_F = -1.25 \text{ eV}$  relative to the vacuum level (which is taken as the energy zero in this paper). From the resulting surface band structure, shown in Fig. 2 before and after cesiation, we learn that the Cs valence electron goes into states lying above the gap in the O-C band complex. Quasicircular electron pockets at the Brillouin zone center  $\bar{\Gamma}$  and corner  $\bar{M}$  are occupied. The three occupied  $\bar{\Gamma}$  pockets consist of Cs  $s + O s$  states, with some C  $p$  character from the first C layer, whereas the two  $\bar{M}$  pockets have strong Cs  $d$  character.

Since the EA involves the placement of unoccupied states, the inability of density-functional-based calculations to give the true band gap (in essence, the position of the unoccupied states) in semiconductors such as diamond must be addressed. The solution is to calculate the dynamic self-energy [14], but probably there is no code in existence that can handle the many-body problem for this surface. Some enlightened speculation is possible, however. (1) Local density approximation calculations do well at reproducing work functions at surfaces, so the partially occupied surface states and the Fermi level should be reasonably accurate. (2) Self-energy calculations do not produce strong changes in gaps between occupied states such as occurs for the fundamental gap between occupied and unoccupied states. In addition, the surface region is metallic and the enhanced screening will reduce self-energy corrections. Thus the valence bands

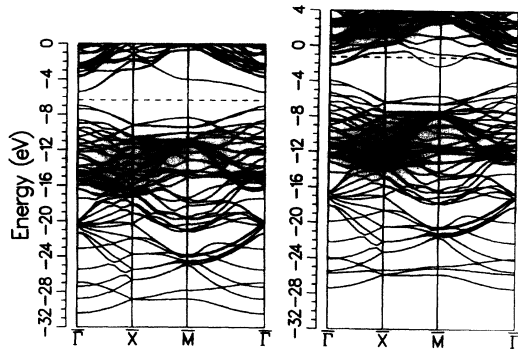


FIG. 2. Surface band structure of C(100):O without (left) and with (right) the  $c(2 \times 2)$  Cs overlayer, along high symmetry directions. The vacuum levels (taken as the zero of energy) are aligned, illustrating clearly the raising of the bands by the addition of Cs. States just below the gap have strong O  $p$  character, and the states just above the gap are discussed in the text. The dashed line in the figure on the right is the Fermi level.

(surface and bulk) in Fig. 2 should be realistically placed. (3) In the bulk the self-energy correction will reproduce the experimental gap. Since the valence bands are properly placed [item (2)] the conduction bands will be raised by the necessary amount. From (1)–(3), the primary effect of self-energy corrections will be simply to raise the bulk CB minimum up to a position in accordance with the known gap. This is the justification for invoking the experimental gap value (which is also the theoretical gap when the self-energy is included [15]) in assigning the position of the CB minimum.

We now consider the behavior of this surface as a NEA emitter. There are empty surface states in the Cs and O layers lying between the bulk CB minimum and the vacuum level (indeed, below the vacuum level, down to  $E_F$ ). In diamond, the CB minima are along the [100] directions. An electron at CB minimum either has its momentum parallel to the (100) surface, in which case it will never escape regardless of the surface properties, or it is perpendicular to the surface. In the latter case the presence of available surface states above  $E_F$  may provide some trapping, but there is no reason to expect a very narrow layer of available states to strongly inhibit transmission through the surface layer. On the contrary, the metallic surface may finally enhance emission, by conducting away charge at the surface that would otherwise be trapped so it does not impede electron transport from the interior to, and through, the surface region.

A particularly important question is how strongly the Cs atoms are bound to the surface; if the bonding is weak the system would not be robust. Geis [9] found his oxygenated diamond surface after cesiation to be very stable, but the structure was unknown. By performing total energy calculations for the cesiated and

uncesiated surfaces, for the Cs overlayer alone, and for isolated Cs atoms, we obtain a binding energy for the Cs monolayer of the 1.34 eV/Cs atom. This binding energy is significantly more than the 0.83 eV/atom cohesive energy of Cs metal, which indicates a stability of the flat surface against Cs cluster formation.

As in the cases of Cs and BaO adsorbed on Tm surfaces, the resulting dipole involves a combination of competing contributions, which makes it difficult to identify any specific charge transfer or rearrangement as the dominant effect in creating the large surface dipole that produces NEA. A detailed analysis of the surface dipole will be published elsewhere. A plot of the charge rearrangement, referred to a Cs monolayer plus the oxygenated C(100) surface, is included in Fig. 1, and the planar averaged charge rearrangement is shown in Fig. 3.

Some features related to dipole formation are clear. First, the difference electron density is positive above the Cs atom, opposing the net dipole. From similar behavior in the Ba-O on W system [8], this effect is attributed to the repulsive interaction of the Cs  $5p$  semicore states (at  $-13$  eV) by bonding C-O states at that energy. Second, there is a negative/positive dipole layer between the Cs and O layers arising from primarily Cs  $d$ -O  $p$  hybridization that contributes strongly to the net dipole. Third, there is a large negative contribution centered on the outermost C atom, again opposing the net dipole. Perhaps the most remarkable aspect of the dipole formation is that the charge rearrangement extends over almost 10 Å, which may be attributed to charge transfer into strongly covalent states and very poor screening perpendicular to the surface.

Comparing the local densities of states (LDOS) in Fig. 4 with those when the Cs is absent (not shown) reveals that the presence of Cs perturbs the C and O LDOSs above the gap by very little, so that filling of these states up to  $E_F$  indicates transfer of Cs charge into the preexisting C-O antibonding states. Clearly from the LDOS in Fig. 4 substantial charge remains on the Cs atom. From the computational starting point of spherical

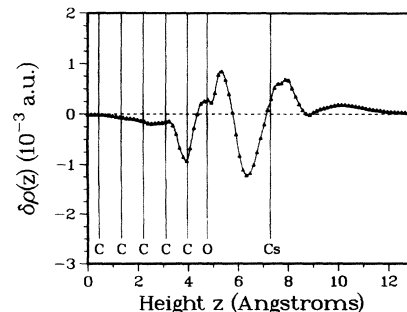


FIG. 3. In-plane average, across one-half of the slab, of the difference density shown in Fig. 1, illustrating the complicated shift in charge that results from cesiation of the C(100):O surface.

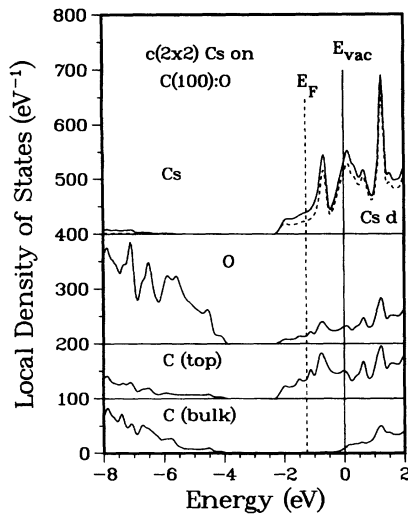


FIG. 4. Local densities of states in the gap region, indicating that some of the Cs valence electron is contributed to the O and uppermost C atoms. About 70% of the occupied Cs density is in  $6d$  (rather than  $6s$ - $6p$ ) states. C(bulk) is the average of the inner eight C layers of the slab.

atoms to self-consistency, 0.04 electron leaves the large Cs sphere and 0.12 electron accumulates in the O sphere. Since a shift of 0.08 electron over a distance of 2.5 Å (the Cs-O layer separation; see Table I) accounts for a dipole of  $\sim 1.5$  eV, ionic charge donation may account for roughly half (and possibly more) of the 3.35 eV dipole.

Recent work on alkali overlayers on metal surfaces provides insight into the current problem. Calculations by Ishida and Terakura [16] and photoemission studies by Wertheim, Riffe, and Citrin [17] indicate that hybridization of adatom and substrate valence states is at least as important as is charge donation in the formation of the dipole. The present results (Figs. 1, 3, and 4) are consistent with such a picture. Ishida and Terakura also find that the dipole can increase with decreasing coverage (to a point); this is encouraging because the coverage level studied here might be difficult to obtain in practice.

The fact that there is strong O and C character in the occupied surface states indicates that the Cs conduction electron enters a complex of hybridized bands with the important distinction that they lie to a considerable extent within the surface rather than simply extending from the surface. This characteristic may make the surface

chemically inactive and physically robust such as was found by Geis [9] and thus more viable commercially.

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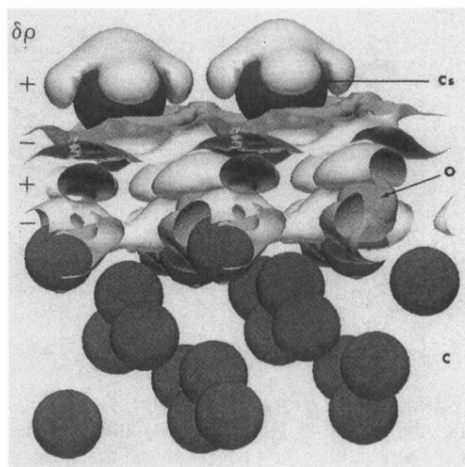


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