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# Effect of carbon vacancies on carbide work functions

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The transition-metal carbides are commonly formed with a substantial density of carbon vacancies. Here we examine the effect of carbon vacancies on the surface properties, primarily the work functions, of HfC and TaC. The method used is a full-potential linear-muffin-tin-orbital formulation, with a supercell approach for obtaining variations in the vacancy distribution. We find that the differing signs of the vacancy-induced changes in the work functions of HfC and TaC are essentially determined by the differing effect of vacancies on the relative position of the Fermi energies in the two materials.

## I. INTRODUCTION

While there has been substantial work on carbide surface properties, theoretical calculations[1–3] involving these surfaces have been confined to stoichiometric carbides, whereas, in practice, most carbide compounds contain an appreciable number of carbon vacancies. The presence of vacancies can be expected to have an effect on surface properties, and of particular interest is their apparent effect on work functions. For example, theoretical calculations[2,3] of the TiC(001) surface have obtained a work function of about 4.6 eV, while measured values have been reported[4] between 3.8 and 4.1 eV. The most likely explanation for the discrepancy would seem to be the existence of vacancies in the experimental samples not included in the calculations. More recently, Gruzalski, Liu, and Zehner[5] have described detailed experimental results for the dependence of the work function on the carbon vacancy density for both HfC and TaC, and reported that they found opposite effects in these two materials. The work function of TaC was found to increase with increasing vacancy density, while the work function of HfC decreased as the number of vacancies was increased. We have completed electronic-structure calculations of both the HfC and TaC surfaces, for several different vacancy densities and distributions, and have examined the vacancy-induced changes in work functions and other surface properties. The method of calculation used is a full-potential, linear-muffin-tin-orbital (LMTO) technique[6,7] which has given reliable results for surface properties, including work functions. The method requires three-dimensional periodicity, and so a repeated slab arrangement is employed in surface calculations.

## II. RESULTS

The atomic arrangement used in these calculations contains repeated five-layer slabs, with (001) surfaces of the rocksalt structure. A unit cell four times as large as required for a stoichiometric crystal was used, giving a total of 40 atomic sites (20 carbon sites) per unit cell. This allows a number of choices for the density and placement of carbon vacancies, and four such choices were studied. (The relative locations of the vacancies are given by Fig. 1, as described in the caption.) One arrangement has no vacancies at all. The second contains two carbon vacancies per unit cell, one on each surface of the five-layer slab. The motivation for this choice is that it allows, as nearly as is possible in this supercell arrangement, examination of an isolated vacancy at the surface. This vacancy distribution has a 25% carbon vacancy density in the surface layers and an overall carbon vacancy rate of 10%. The third vacancy arrangement also contains two vacancies per unit cell, both in the center layer, and was chosen to provide direct comparison between

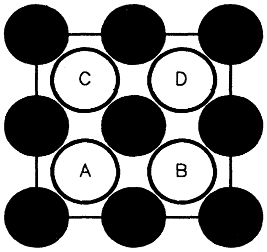

FIG. 1. This figure shows the atomic arrangement of a single layer within the unit cell. In the center and surface layers of the five-layer slab, the solid circles represent transition-metal atoms, and the open circles represent carbon. In the two subsurface layers, the roles are reversed. For one surface vacancy per surface layer (arrangement 2) the carbon located at *D* is removed from each surface layer. The third arrangement of vacancies has two carbons removed, from the *C* and *B* locations of the center layer. The fourth arrangement has locations *C* and *B* vacated in the center layer and locations *A* and *D* vacated in the two surface layers.

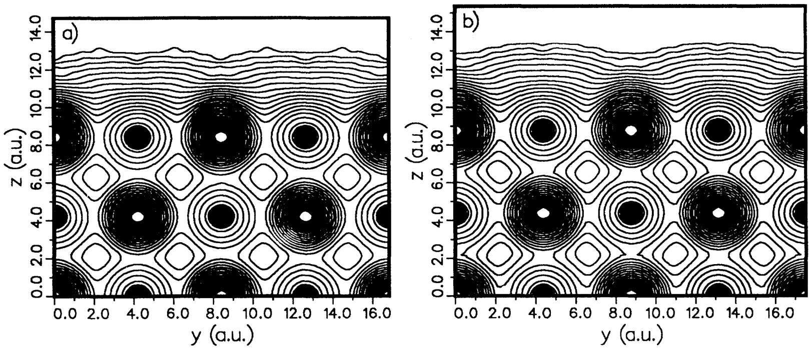

FIG. 2. Total electron density of (a) tantalum and (b) hafnium carbide surfaces shown in a (010) cross section. Neighboring contour lines differ in density by a factor of $\sqrt{2}$.

bulk and surface vacancies. The fourth vacancy distribution contains two vacancies in each of the surface layers and the center layer, giving an overall vacancy rate of 30% and a vacancy rate of 50% in the surface layers. Of the four arrangements, the fourth most resembles a sample with a uniform distribution of vacancies. Calculations were performed for TaC in each of these four structures, and for HfC in the first (no vacancies) and fourth (center and surface) vacancy arrangements.

The calculated work functions are given in Table I, along with the reported experimental results. Also listed in Table I are calculated results[7] for stoichiometric TaC using the minimal size 5-layer unit cell (ten atomic sties), with and without surface relaxation included. The calculation with relaxation included shows good agreement with experiment, while neglect of relaxation (as was done in the present work using the 40-atomic-site cell) results in work functions which are somewhat smaller than experiment. This appears to be the case for HfC as well. Nonetheless, the table shows that the calculated changes of work function, due to the introduction of vacancies, reproduce the experimental changes both in magnitude and sign. The experimental results for TaC, with a vacancy density of approximately 50%, give an increase in work function of 0.35 eV. The calculated TaC results with overall vacancy densities of 10%, 10%, and 30% (surface layer vacancy densities of 0%, 25%, and 50%; the second, third, and fourth arrangements described above) show changes in the work function of $-0.04$, $+0.04$, and $+0.27$ eV, respectively. The experimental results for HfC show a decrease of the work function with increasing vacancy density: a vacancy density of approximately 40% resulted in a decrease of the work function by 0.76 eV. The calculated HfC result, with a net vacancy density of 30% (surface layer density of 50%), shows a decrease in work function of 0.96 eV. Given the uncertain relationship between the experimental vacancy distributions and ours, this represents quite satisfactory agreement between the measured and calculated changes in work function. (It should be noted that the preparation of nonstoichiometric surfaces described in Ref. 5 resulted in both a modified atomic structure and an uncertain distribution of the vacancies within the near-surface region.)

To identify the origin of this difference in behavior between HfC and TaC, we begin by presenting the calculated total electron densities in Figs. 2–4. Figure 2 compares the electron densities of stoichiometric TaC and HfC, and minor differences between the two surfaces can be seen. For example, while both surfaces show a substantial corrugation of charge density near the surface, this is more pronounced in the case of HfC. What is relevant to the changes in work function, however, is how these charge distributions, and the associated electric-dipole moment at the surface (or surface barrier), change with the introduction of carbon vacancies.

Figure 3 shows the TaC surface with center layer vacancies and with surface layer vacancies, and Fig. 4 shows both the TaC and HfC surfaces with center and surface layer vacancies. (The center layer vacancies in Fig. 4 do not lie in the same plane as the surface vacancies and so do not appear in the figure.) From Fig. 3, the density in the interior region of the surface vacancies is very similar to that of the center layer vacancies. (Comparison of the total energies with two surface vacancies and two center layer vacancies allows an estimate of the

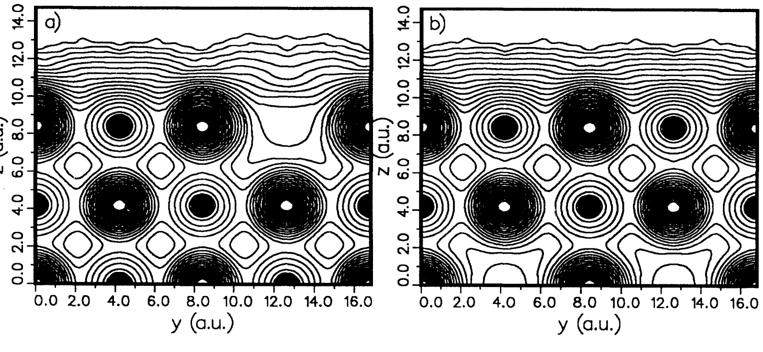

FIG. 3. Electron density of the TaC surface with (a) surface layer and (b) center layer vacancies.

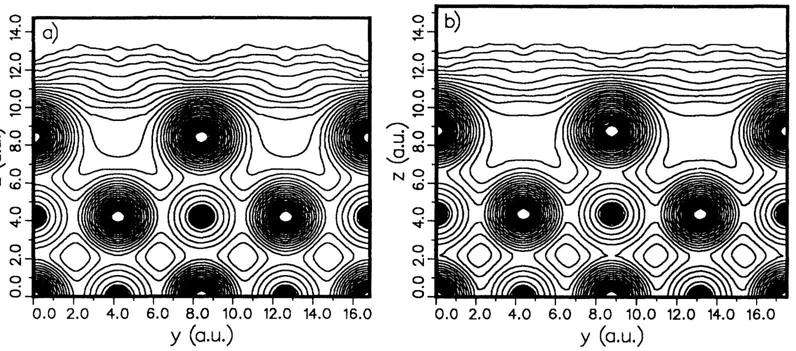

FIG. 4. Total electron density of (a) tantalum and (b) hafnium carbide surfaces with surface layer and center layer vacancies present. (The center layer vacancies do not lie in the plane of the figure.)

energy required to move a vacancy from the bulk to the surface of TaC. Our results give a value for this of 0.25 eV.) As can be seen in Figs. 3 and 4, there are no dramatic changes in the form of the electron-density tail extending into the vacuum, and also no obvious differences in how the charge densities of these two materials respond to the presence of vacancies This would suggest, solely on the basis of the visible appearance, that changes in work function are not dominated by changes in the surface dipole moment, and moreover, that the changes in HfC and TaC dipole moments are similar. As the work function is the difference between the Fermi energy and vacuum potential, this implies that differences in work-function behavior are due to the changes in Fermi energy.

Figure 5 gives the total density of states of TaC for three of the vacancy arrangements, while Fig. 6 shows two of the corresponding densities of states for HfC. The energy scale of the graphs has been extended to include some of the core states. The dashed vertical line marks the Fermi energy, while the open arrow indicates the vacuum level. The work function is simply the energy difference between these two points. It is important to realize, in comparing these figures, that they describe different materials, and so there is no common reference energy or potential in the interior of the material: that is there is no definition of a zero of potential which remains fixed relative to the material as vacancies are created.

TABLE I. Calculated and experimental work functions for TaC and HfC. Numbers in parentheses are differences from the corresponding stoichiometric values. The experimental values are from Ref. 5. All units are in eV.

| | TaC | HfC |
|---|---|---|
| Experiment | | |
| Stoichiometric | 4.38 | 4.63 |
| Nonstoichiometric | (+0.35) | (−0.76) |
| Calculated | | |
| Small cell (10 atom) | | |
| Relaxed | 4.24 | |
| Unrelaxed | 3.86 | |
| Large cell (40 atom) | | |
| (1) No vacancies | 3.84 | 4.31 |
| (2) Center vacancies | (−0.04) | |
| (3) Surface vacancies | (+0.04) | |
| (4) Surface and center vacancies | (+0.27) | (− 0.96) |

Thus the question of whether the work function has decreased because the Fermi energy has gone up, or instead because the vacuum barrier has decreased, is not uniquely defined. Nonetheless, useful qualitative distinctions can still be made. From the density-of-states (DOS) figures, it is clear that whether the zero of energy is determined from the "muffin-tin zero" (the average potential in the interstitial), or the first moment of core levels (marked by solid arrows), the same conclusions are reached: the energy difference between the vacuum level and the major features of the DOS decreases a moderate amount in *both* HfC and TaC. So it is qualitatively

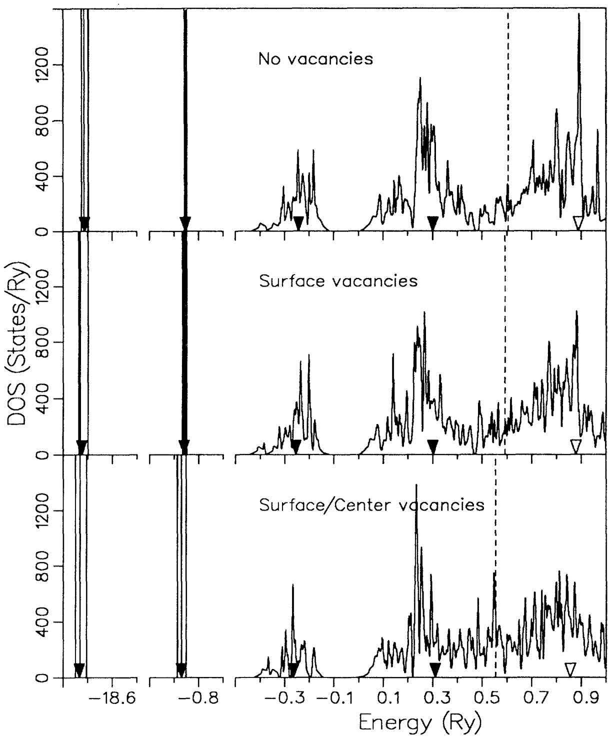

FIG. 5. The total density of states in TaC with three vacancy arrangements, with energies measured relative to the muffin-tin zero. Two core levels are included, the carbon 1$s$ levels (around −18 Ry) and the Ta 4$f^{7/2}$ levels (around −0.8 Ry). The dashed lines give the Fermi energies, the open arrows give the position of the vacuum potentials, and the solid arrows give, in order, the first moment of the C 1$s$ and Ta 4$f^{7/2}$ core states, the C 2$s$ band, and the occupied part of the valence band.

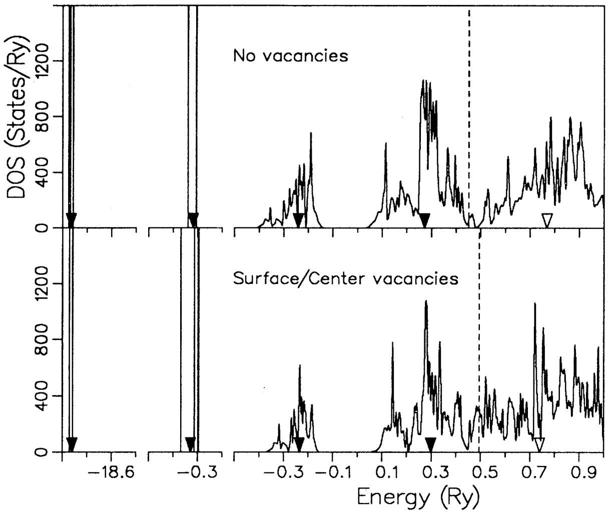

FIG. 6. The total density of states in HfC for two arrangements of vacancies. The description of the features of the figure is the same as for Fig. 5.

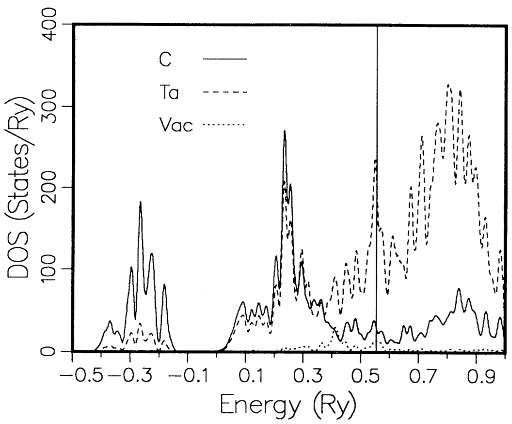

FIG. 7. The partial densities of states in TaC with surface and center vacancies, weighted according to amount of charge in the carbon, tantalum, and vacancy spheres.

correct to say that vacancies reduce the potential barrier between the interior of the material and vacuum in both materials. On the other hand, vacancies induce a marked change in the energy difference between the features of the density of states and the Fermi energy, with the relative Fermi energy moving *up* in HfC and *down* in TaC, for reasons that are quite clear on considering the behavior in the figures. The total densities of states in the cubic carbides are all quite similar, with the lower part of the valence band composed of covalent bonding orbitals of carbon *p* states and transition-metal *d* states, separated from the remainder of the valence band (composed primarily of antibonding and delocalized transition-metal *d* orbitals) by a sharp minimum in the total density of states. In the transition-metal carbides composed of fourth-column transition metals such as hafnium and titanium, the Fermi energy lies directly in the center of this minimum, while the fifth-column transition metals (such as tantalum) form carbides with the Fermi energy somewhat above the minimum (to accommodate the one additional electron per unit cell). In both cases, as can be seen in Figs. 5 and 6, the introduction of vacancies washes out the bonding-antibonding structure, and the minimum in the density of states is progressively filled in. As a result, column-four transition-metal carbides have their Fermi energies moved upward by the introduction of vacancies: in effect the Fermi energy must follow the net number of states which have moved above the old Fermi energy from below. And in a corresponding manner, the fifth-column carbides have their Fermi energies lowered by the introduction of vacancies, since the Fermi energies must follow the states which have moved below them. Both Fermi energies appear to move by roughly the same amount; however, since both surface barriers have decreased, the result is a modest increase in the TaC work function and a larger decrease in the work function of HfC. Relative to the muffin-tin zero, the values of these changes from the no-vacancy to the surface and center vacancy arrangement are as follows: The vacuum potential decreased in both the HfC and TaC cases by about 0.4 eV, while the Fermi energy in HfC increased by about 0.6 eV, and the Fermi energy in TaC decreased by about 0.7 eV.

Finally, Fig. 7 gives the muffin-tin sphere projected density of states in TaC with surface and center vacancies (corresponding to the bottom panel of Fig. 5), and it can be seen that the new states in the gap are largely Ta-dominated states (of *d* character), which have arisen from the destruction of the covalent bonds (and antibonds) between carbon and transition-metal atoms. This destruction of bonds induces a transfer of charge to tantalum sites,[8] and results in the shifts in some core levels which are apparent in Figs. 5 and 6. It is worthwhile to note that while vacancies can destroy the bonding-antibonding structure, creation of the (001) surface by itself does not.

## III. SUMMARY

We have calculated, using a full-potential LMTO method, the electronic structure of hafnium carbide and tantalum carbide surfaces with and without carbon vacancies present. In good agreement with experiment, we find that vacancies increase the work function of TaC but decrease the work function of HfC. An examination of the density of states led to the conclusion that these changes in work function were essentially due to the change in relative Fermi energy accompanying creation of vacancies, with the Fermi energy moving up in HfC, down in TaC. This is in agreement with the conclusions, based on the experimental data, reached by Gruzalski, Liu, and Zehner. This also appears to reconcile the calculated work function of stoichiometric titanium carbide with the lower experimental values, since Ti is also a fourth-column transition-metal element, and TiC can be expected to show behavior similar to that of HfC.

## ACKNOWLEDGMENTS

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