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Bonding of α-SiC basal planes to close-packed Ti, Cu, and Pt surfaces: Molecular-orbital theory

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An atom-superposition–electron-delocalization molecular-orbital study of the binding of α-phase (hexagonal) silicon carbide (0001) Si and $(000\bar{1})$ C basal planes to the close-packed surfaces of titanium, copper, and platinum has been made using $Si_{13}C_{13}H_{25}$ and M_{31} (M denotes metal atom) clusters. The interfacial binding is generally characterized by charge transfer from the metals to half-filled band-gap surface dangling orbitals and molecular-orbital stabilizations involving these orbitals. Both of the silicon carbide surfaces are predicted to bind strongly to these metals.

INTRODUCTION

The gaining of an understanding of bonding at metal-ceramic interfaces is of potential importance to the development and improvement of electronic devices and composite structural materials. In recent studies we examined, using cluster models and molecular-orbital theory, the electronic properties of Al_2O_3 and Ni (Ref. 1) and Pt (Ref. 2) surfaces and characterized the bonding at several possible metal alumina interfaces. In Ref. 2 we discussed the handful of experimental studies in the literature[3-11] and found little was known about the actual metal-alumina interphase structures and compositions. There is even less experimental literature on the bonding of silicon carbide, SiC, to metals. Such systems are the topic of this paper.

We have chosen the close-packed Ti(001), Cu(111), and Pt(111) metal surfaces and the C-terminated $(000\bar{1})$ and Si-terminated (0001) surfaces of hexagonal (α) SiC for this theoretical investigation. Titanium is a possible structural composite material; copper is a possible conductor in electronic devices using silicon carbide; and platinum is widely studied in metal-ceramic seal applications.

In our theoretical study of α-Al_2O_3/Pt(111) bonding we found that empty dangling s-p hybrid orbitals with energies in the O^{2-}-Al^{3+} band gap were centered on Al_2O_3 basal-plane cations.[2] These planes have $\frac{1}{2}$ of the cations missing because of the stability of maintaining stoichiometry and charge balance. The Pt(111) surface was predicted to adhere strongly to the alumina basal plane by means of donation bonding from the Pt atoms to the dangling surface orbitals on the surface Al^{3+}. Though individual O^{2-}—Pt^{+} bonds were calculated to be weaker than the Al^{3+}—Pt bonds, their greater number per unit area suggested adhesion would be strongest in an oxidizing atmosphere. Band-gap surface orbitals on silicon carbide should also be s-p hybrids and the surface bands should be half-occupied. Since Si is more electropositive than C, its (0001) surface band should lie higher in energy than the $(000\bar{1})$ C surface band. These bands should be able to accept charge from the metal substrates, as in the case of alumina-platinum[2] or CO 5σ donation bonding to Zn^{2+} on ZnO.[12] Unlike these examples, the surface bands can also donate charge to the metals because they are half-occupied. Si should be a better donor and poorer acceptor than C.

Reaction bonding of ceramics and metals occurs at temperatures several hundred degrees below the melting points of the metals.[3-11] Copper, titanium, and platinum melt at 1083, 1668, and 1769 °C, respectively, and silicon carbide sublimes and decomposes at >2000 and 2210 °C. Consequently, past low-energy electron diffraction spectroscopy (LEED) and Auger-electron spectroscopy (AED) studies of heat-treated (0001) and $(000\bar{1})$ α-SiC surfaces are of interest. It has been thus found by van Bommel *et al.*[13] that a monocrystalline graphite monolayer is formed on the Si surface by a Si evaporation mechanism upon heating to 800 °C. Polycrystalline graphite formation was observed to begin at a lower temperature on the C surface. It might be expected that graphite, a lubricant, would affect the adhesion of silicon carbide to metals.

Chamberlain[14] has examined, using x-ray diffractometry and Auger spectroscopy, the solid-state reaction of Ti thin films with α-SiC basal-plane surfaces. On annealing to 571–800 °C, C and Si were released and TiC_x ($x<1$) formed by diffusion into the Ti film but titanium silicides were not detected.

Bermudez,[15] in an Auger and electron-energy-loss spectroscopy (EELS) study of Al deposition on disordered (0001) and $(000\bar{1})$ α-SiC surfaces, found Al island formation at room temperature. On annealing to ≤ 600 °C the Al partially segregated to C-rich surface sites. Annealing to 700 °C caused Al_4C_3 to form but aluminum silicide was not observed to form.

On the basis of the studies by Chamberlain and Bermudez, it appears that annealing to ~ 600 °C is likely to cause metal carbide formation at metal-SiC interfaces. A study of this process, though interesting and important, is beyond the scope of the present paper. We will model the bonding between idealized smooth surfaces such as might occur when pressing the ceramic and metal together at temperatures below 600 °C.

Another variable is the atmosphere under which reaction bonding is carried out. The above studies were done under UHV, essentially a reducing condition. The surface of SiC is well-known to oxidize massively when exposed to O_2 at 1130 °C to form an overlayer of SiO_2 and CO gas.[16] The effects of oxygen on SiC-metal bonding at lower temperatures are not known and are beyond the scope of the present theoretical study.

THEORETICAL METHOD

We use the semiempirical atom-superposition and electron-delocalization molecular-orbital (ASED-MO) theory and cluster models to carry out our study of SiC bonding to the Ti, Cu, and Pt surfaces. Thus our approach is the same as was used for Al_2O_3/Pt bonding in Ref. 2. In the atom-superposition–electron-delocalization molecular-orbital (ASED-MO) theory the molecular binding energy is equal to the integral of electrostatic forces on the nuclei as the atoms come together to form the molecule.[17] The molecular electronic-charge-density distribution function is partitioned into atomic components associated with atom superposition and the remainder, which is due to electron delocalization. The atom-superposition components are calculated directly using atomic valence-electron orbitals and the electron-delocalization energies are approximated as the difference between one-electron valence-orbital energies of the molecule and the atoms.[18] The molecular orbital energies are determined using a Hamiltonian similar in form to extended Hückel and depend on atomic valence ionization potentials and valence-Slater-orbital exponents. The energies of the atoms are determined using atomic valence ionization potentials. Parameters used in this work may be seen in Table I. The Pt parameters were used in Ref. 2 and those for Ti and Cu are based on literature sources for valence ionization potentials,[19] $s \rightarrow p$ excitation energies,[20] and exponents.[21] Since the parameters of the ASED-MO theory depend on measured valence-state ionization potentials and valence exponents that are adjusted to yield diatomic bond lengths, they implicitly include the effects of relativistic core contraction which occurs in Pt. Standard adjustments were made to approximate charge self-consistency for SiC. Using the diatomic SiC molecule, the Si valence-state ionization-potential parameters were increased by 0.1 eV steps and simultaneously those for C were decreased by 0.1 eV steps until the final charge transfer from SiC (0.16) was close to that predicted by the ionicity vs electronegativity difference relationship of Pauling (0.12). On top of this, the literature C valence-Slater-orbital exponents were decreased by 0.1 a.u. so that the predicted bond length (1.62 Å) was reasonable (an experimental value is unavailable). This decrease is a result of charge transfer and it increases the two-body atom superposition energy which is calculated using the atomic density function of the more electronegative atom and the nucleus of the other atom of each pair.[18]

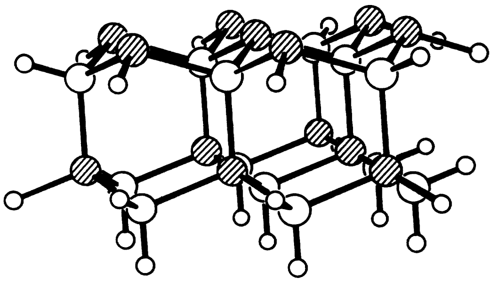

FIG. 1. $Si_{13}C_{13}H_{25}$ model of (0001) and (000$\bar{1}$) SiC surfaces. Small spheres are H atoms. Shaded spheres are either Si or C and the others are, correspondingly, either C or Si.

Two-layer-thick 31-atom clusters were used to model the (001) Ti and (111) Cu and Pt surfaces. The bulk nearest-neighbor spacings, which are, respectively, 2.95, 2.56, and 2.77 Å were assumed. A high-spin model was used for the metal clusters with each d-band orbital occupied by at least one electron. This resulted in 118 half-filled cluster orbitals at the top of the d band for Ti and 22 for Pt. Cu has a filled d band and there is one unpaired electron in the cluster. The $Si_{13}C_{13}H_{25}$ clusters used to represent the (0001) Si-terminated and (000$\bar{1}$) C-terminated surfaces of α-SiC are shown in Fig. 1. The cluster has an idealized wurtzite structure (see Wyckoff[22]) with nearest-neighbor Si—C bond lengths of 1.88 Å. Si-H and C-H distances of 1.52 and 1.12 Å, respectively, were used. The top (bottom) layer has seven Si (C) atoms while the middle two layers have six C (Si) atoms. In the seven-atom layer the central face atom is threefold coordinated and the six edge atoms are twofold coordinated. In the middle layers there are three fourfold-coordinated

TABLE I. Atomic parameters used in the calculations. Principal quantum number n, ionization potential V_{IP} (eV), Slater-orbital exponent ζ (a.u.), and linear coefficients c, for double-ζ d functions. The text explains their sources. The top Pt layer V_{IP} values were increased 0.1 eV from these as in Ref. 2.

	s			p			d					
Atom	n	V_{IP}	ζ	n	V_{IP}	ζ	n	V_{IP}	ζ_1	c_1	ζ_2	c_2
Ti	4	6.8	1.50	4	4.85	1.20	3	8.00	4.55	0.4391	1.60	0.7397
Cu	4	7.73	1.85	4	3.94	1.55	3	10.40	5.95	0.6255	2.20	0.5542
Pt	6	9.00	2.55	6	4.96	2.25	5	9.60	6.013	0.6334	2.696	0.5512
C	2	15.29	1.5083	2	9.96	1.4679						
Si	3	14.76	1.6344	3	9.45	1.4284						
H	1	13.6	1.200									

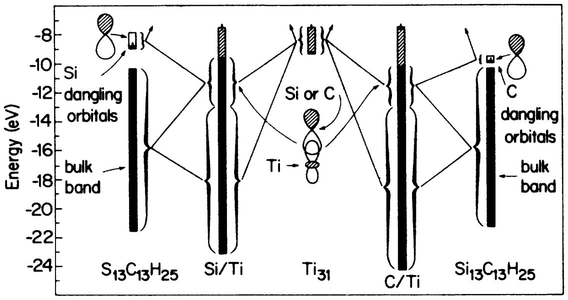

FIG. 2. Bonding of $Si_{13}C_{13}H_{25}$ clusters to Ti(001).

TABLE II. Heights h (Å) and binding energies per C or Si surface atoms, E_B (eV), calculated for C and Si surface faces of $Si_{13}C_{13}H_{25}$ clusters bonded to 31-metal-atom cluster.

	Ti	Cu	Pt
		C surface	
h	2.0	2.1	2.0
E_B	4.5	3.0	2.5
		Si surface	
h	2.4	1.9	2.1
E_B	3.5	3.8	3.2

bulklike atoms and three threefold-coordinated edge atoms. These clusters have one unpaired electron.

RESULTS AND DISCUSSION

The calculated electronic structures for the Si-covered and C-covered surfaces are included in Fig. 2. Energy levels in the bulk band gap correspond to dangling s-p hybridized surface orbitals. These band gap bands are half-filled. The C surface band is 0.45 eV wide and its bottom lies 0.33 eV above the bulk valence band. The Si surface band is higher and wider, with a width of 1.14 eV and its bottom lying 1.32 eV above the bulk valence band. This means the C surface will have relatively poor electron donating abilities and relatively good electron accepting abilities when compared to the Si surface.

It might be supposed that the empty dangling orbitals on the C surface could become filled due to the widening of the valence band if the cluster size were increased indefinitely to better represent the surface of a bulk. In fact, we have made a bulk band calculation using the ASED-MO Hamiltonian[23] and find the top of the valence band is 0.9 eV above the highest dangling surface band level for $Si_{13}C_{13}H_{25}$ cluster. Naively, this means the C surface orbitals would become completely occupied. However, this would require a long-range polarization of the bulk which is physically questionable. Only an accurate charge self-consistent calculation would give a definitive answer to this. We expect that our cluster model is thick enough to include applicable long-range effects and therefore, though it is not charge self-consistent, it should represent the surface electronic structure satisfactorily for our purposes.

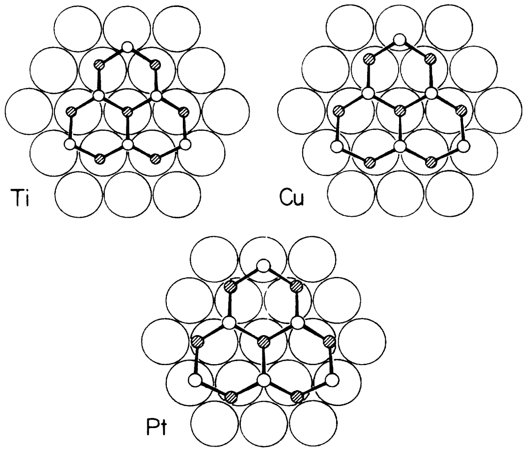

FIG. 3. Interfacial structures used in the calculations. H atoms and the SiC sheet nearest the viewer are omitted.

We have studied interfacial bonding with these clusters by bringing them together as shown in Fig. 3., with 119, 0, and 23 unpaired electrons for the Ti, Cu, and Pt/SiC systems, respectively. Predicted interfacial distances and binding energies per interfacial C and Si atom are in Table II. From these results, C bonds more strongly than Si to Ti but for Cu and Pt the metal-silicon bonds are stronger. For all three metals the bonds to silicon are relatively close to one another in strength and the Pt—C bond is especially weak.

The C and Si surface band-gap orbitals interact with the metal band orbitals, the net result being donation into them from the metals as given in Table III. The empty C surface orbitals, being lower in energy, accept more charge from each of the metals than Si. Cu is a slightly better donor of charge than Ti and Pt is considerably weaker than either. These relative results can be understood from the orbital correlation diagrams, Figs. 2, 4, and 5. The top of the Cu band lies slightly above the top of the Ti band, and the top of the Pt band lies below either.

TABLE III. Average charge for surface Si and C atoms of the $Si_{13}C_{13}H_{25}$ cluster models of the (0001) and $(000\bar{1})$ SiC surfaces before and after bonding to 31-atom cluster models of close-packed Ti, Cu, and Pt(M) surfaces.

	Ti	Cu	Pt
Si	0.40	0.40	0.40
Si/M	0.07	0.03	0.34
Difference	−0.33	−0.37	−0.06
C	−0.49	−0.49	−0.49
C/M	−0.85	−0.97	−0.70
Difference	−0.36	−0.48	−0.21

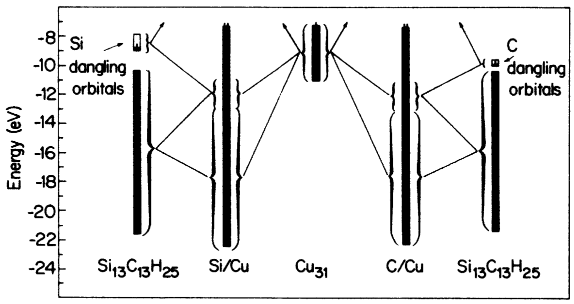

FIG. 4. Bonding of $Si_{13}C_{13}H_{25}$ clusters to Cu(111).

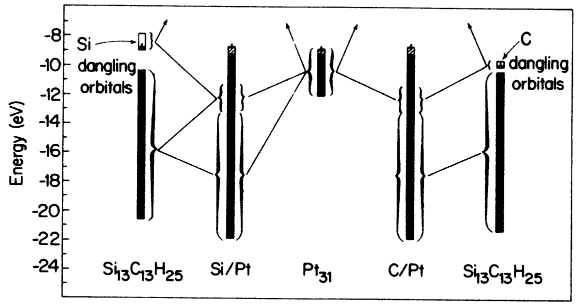

FIG. 5. Bonding of $Si_{13}C_{13}H_{25}$ clusters to Pt(111).

The dangling surface orbitals enter into bonding molecular orbital combinations with metal valence-band orbitals, as shown in Figs. 2, 4, and 5. Orbitals involving the metals and surface Si and C atoms are also to be found at lower energies as well. These are caused by the mixing of filled SiC bulklike orbitals which have surface atom contributions with the metal orbitals. These interactions are shown schematically in the figures.

CONCLUSIONS

From the above it is to be concluded that smooth silicon carbide basal-plane surfaces should bind strongly not only to Ti, Cu, and Pt but to most transition metals because the charge transfer and orbital stabilizations will occur for other metals. The formation of TiC_x on annealing a SiC/Ti interface to 571–800 °C as observed by Chamberlain[14] is consistent with our prediction of strong Ti—C bonds. However, this and other side reactions, such as those involving O_2, are, at the high temperatures employed for reaction bonding, largely the consequences of bulk thermodynamic stabilities. It is therefore important to study these interfaces experimentally to determine actual interfacial structures and compositions. Such information would allow more detailed theoretical modeling.

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