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Molecular view of the interfacial adhesion in aluminum-silicon carbide metal-matrix composites

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The binding energies, electron charge transfer, bond lengths, and core level shifts of Al-Al, Al-Si, Al-C, and Si-C dimers have been calculated self-consistently using the linear combination of atomic orbitals-molecular orbital theory. The exchange interactions are treated using the unrestricted Hartree-Fock theory and correlation corrections are included through the Möller-Plesset perturbation scheme up to fourth order. The results are used to understand the nature and strength of bonding at the interface of Al and SiC crystals. The strong bonding of Al-C dimers compared to Al-Al and Al-Si is shown to be responsible for the aluminum carbide formation at the interface. The charge transfer between the constituent atoms in the dimer and the accompanying core level shifts are also shown to be characteristic of what has been observed at the Al/SiC interface.

The importance of metal-matrix composites in modern technological applications has led to many experimental¹ and theoretical^{2,3} studies in recent years. Despite these numerous efforts, a fundamental understanding of the nature of bonding at the interface still remains an elusive problem. Experimentally, the composition at the interface and the interfacial binding energy are hard to evaluate directly. Theoretically, the lack of a precise picture of the atomic arrangements at the interface, the large number of atoms per unit cell, and the possibility of surface reconstruction make any first-principles calculation difficult.

A few attempts^{3,4} have been made recently to study adhesion at the interface from an atomistic point of view. Bermudez⁴ has used spectroscopic methods to study the physical and electronic structure of the interface between Al and SiC. He has found that aluminum deposited at room temperature forms islands randomly distributed over the surface. Upon annealing, Al aggregates at C-rich sites and at high temperature reacts with C (but not Si) to form Al₄C₃. He also has observed a shift in the Al 2*p* level to higher binding energy while the Si 2*p* level goes to a lower binding energy.

In this letter we show that these results can be understood from self-consistent quantum mechanical calculations of Al-Al, Al-Si, Al-C, and Si-C dimers. We find that the binding energy of Al-C is significantly higher than that of Al-Al or Al-Si. This accounts for the aggregation of Al to C-rich sites. The charge transfer between Al and Si is smaller than that between Al and C. In both the cases, however, charge is transferred from the Al site to C and Si sites resulting in a downward shift of the Al core molecular orbital (MO) levels and an upward shift in the C and Si core levels. Our results are compared with available theoretical and experimental results on the dimers as well as with the x-ray photoelectron spectroscopy study⁴ at the Al/SiC interface.

Our calculations are based on the self-consistent field linear combination of atomic orbitals molecular orbital (SCF-LCAO-MO) method.⁵ We treat the electrostatic and the exchange terms of the Hamiltonian for the system us-

ing the Hartree-Fock approximation. The correlation effect is calculated using the Möller-Plesset perturbation scheme up to fourth order.⁵ We have calculated the bond lengths and binding energies for the dimers consisting of all possible combinations of Al, C, and Si. We have used combinations of Gaussian functions to describe the atomic basis sets. For Al, Si, and C we have used (7*s*, 5*p*, 1*d*), (6*s*, 5*p*, 3*d*), and (5*s*, 4*p*, 3*d*) basis, respectively. These are reoptimized subsets of basis functions used by earlier authors.⁶⁻⁸ In Table I, we give our results for the bond lengths and the binding energies and compare them with experiments. Note that the agreement in the binding energies between theory and experiment are in general very good except for AlC. In this case, the theoretical value is much higher than experiment⁹ whereas in all other situations, predictions are less than experiment. In a variational calculation such as ours the calculated binding energy is usually less than the experimental value. It would, therefore, be of interest to repeat the measurement of the binding energy of AlC.

In the literature one can find calculations of the binding energies of Al₂,^{6,10} Si₂,^{7,11} and C₂ (Refs. 8, 11, and 12) where more extensive basis functions than ours have been used. For example, Bauschlicher and co-workers have studied Al₂ (Ref. 6) and C₂ (Ref. 11) using a variety of basis functions and correlation approximations. In Al₂ their basis⁶ included up to *f* functions while in C₂ they used¹¹ up to *g* functions. In Al₂ their calculated values for bond lengths and binding energies lie in the range of 2.72–2.77 Å and 1.081–1.425 eV, respectively. These have to be

TABLE I. Bond lengths and binding energies of dimers formed out of combinations of Si, C, and Al atoms.

System	Bond length (Å)		Binding energy (eV)	
	Expt.	Theory	Expt.	Theory
Al ₂	2.56	2.71	1.55 ± 0.15	1.26
Si ₂	2.25	2.26	3.21	2.83
C ₂	1.243	1.26	6.08	5.26
AlC	1.95	2.00	1.86 ± 0.34	3.19
SiC	1.70	1.71		4.28
AlSi	2.41	2.42	2.60	2.37

compared with the experimental values^{13,14} of 2.73 Å and 1.55 ± 0.15 eV. For C₂ they¹¹ have obtained bond lengths and binding energies in the range of 1.248–1.255 Å and 5.1–6.15 eV, respectively. The corresponding experimental values¹⁵ are 1.31 Å and 6.08 eV. Using a (8s,6p,3d) basis set Kraemer and Roos⁸ have calculated the bond length and binding energy for C₂. Their values of 1.324 Å and 5.79 eV are also in good agreement with experiment. For Si₂ Raghavachari⁷ has obtained a bond length of 2.227 Å and a binding energy of 3.06 eV using a (6s, 5p, 3d, 1f) basis. Using variations of a far richer basis (6s, 5p, 3d, 2f, 1g) and different levels of correlation, Bauschlicher and Langhoff¹¹ have obtained results of 2.238–2.292 Å for bond length and 2.58–3.25 eV for binding energy for Si₂. These are close to the results of Raghavachari.⁷ The corresponding experimental values¹⁴ for Si₂ are 2.25 Å and 3.21 eV which are quite close to the above-mentioned theoretical values. Bauschlicher and Langhoff's bond lengths for SiC¹¹ lie in the range 1.709–1.741 Å which agrees very well with the experimental value¹⁴ of 1.7 Å. No experimental value for the binding energy is available for SiC that can be compared with the calculated values (3.3–4.4 eV) of these authors. We are not aware of any theoretical studies of AlC or AlSi dimers. None of the authors mentioned above have analyzed core level shifts and/or charge transfer between the atoms.

As mentioned earlier, the basis sets used in our calculations are subsets of those used by the above authors. A comparison of our results in Table I with experiment and with the results of these authors clearly indicates that our choice of basis functions can provide results for bond lengths and binding energies that agree equally well with the experiments. In this letter our aim, however, is to study systematically not only the relative binding strength of a series of dimers involving Al, Si, and C but also the charge transfer and core level shifts. The preceding discussion regarding our choice of basis functions and levels of correlation ensures that our results can provide accurate description of the nature of bonding and electronic structure in all the dimers considered.

We note in Table I that the binding energy of the Al₂ dimer is the weakest, whereas that for C₂ is the strongest. This is understandable since C forms a strong covalent bond whereas Al bond is characterized by a metallic behavior. However, what is surprising at first sight is that the AlC bond is stronger than the AlSi bond. Both C and Si have a s²p² configuration in the outermost shell and one would have thought that there would not be much difference in the relative binding.

The overall strength of the AlC bond implies that when an interface is formed between Al and SiC, Al would prefer to bond with a C-terminated SiC matrix. This is in agreement with the annealing studies⁴ where Al was found to aggregate to the C-rich sites. The origin of this preferential bonding can be seen to be due to the increased charge transfer between Al and C than that between Al and Si (see Table II). In both AlSi and AlC, the charge is transferred away from Al sites. The increase in charge transfer in AlC compared to AlSi is responsible for the

TABLE II. Mulliken population and core level shifts (eV) at the atomic sites in different dimers.

Probe atom	System	Mulliken charge	Level shift (eV)		
			1s	2s	2p
Al	Atom	13.00	0.000	0.000	0.000
	Al ₂	13.00	0.109	0.082	0.054
	AlSi	12.79	-0.470	-0.493	-0.511
	AlC	12.53	-0.517	-0.490	-0.462
Si	Atom	14.00	0.000	0.000	0.000
	Si ₂	14.00	-0.346	-0.289	-0.292
	AlSi	14.21	1.036	0.927	0.883
	SiC	13.04	-1.144	-1.137	-1.081
C	Atom	6.00	0.000
	C ₂	6.00	-0.408
	AlC	6.47	2.203
	SiC	6.96	1.691

stronger bond in the former. These charge transfers are followed by a shift in the core level binding energies. The binding energy of a core level increases if charge is transferred away from it because this reduces electron-electron repulsion. On the contrary, the binding energy decreases as electrons are transferred to the atom. These systematics are evident in all the dimers in Table II. A quantitative comparison of the core level shifts with experiments involving x-ray photoelectron or Auger spectroscopy is difficult not only because the atoms are in a solid-state environment but also because a core hole created by a photon could relax as the electron is removed from its immediate environment. However, the systematics of the core level shifts of Al 2p to higher binding and Si 2p to lower binding is in agreement with the experiment⁴ in Al/SiC composite.

It is also possible to analyze the Mulliken population of various levels to get a better understanding of the orbitals that participate in the bonding. The inner 1s and 2s orbitals of Al and 1s orbital of C do not participate much in the bonding and these populations stay at their atomic values. Al loses its charge mostly from the 3s and 3p orbitals and C gains this charge in its 2p state. The average occupancy of the Al 2p orbitals is 1.94. The Al 3s, 3p_x, 3p_y, and 3p_z orbitals have 1.8, 0.15, 0.15, and 0.62 electrons, respectively. The C 2s, 2p_x, 2p_y, and 2p_z are occupied by 1.84, 0.87, 0.87, and 0.89 electrons. The bonding, therefore, is of the sp type. This charge transfer is shown in Fig. 1 by plotting the difference between the electron densities obtained self consistently in the AlC dimer and that obtained by superimposing their free atomic densities. Note that there are positive and negative regions of charge density indicating where electrons have been gained or lost. The electron-rich regions in the vicinity of the Al nucleus are due to the increase in the binding energies of core levels discussed above.

It is possible to understand the systematics in the binding energies and charge transfer in AlSi and AlC even at the atomic level. The energies of the 2p level of C and 3p levels of Al and Si atoms are, respectively, -11.02, -5.71, and -7.62 eV. The strength of bond between two atoms can be influenced by the hybridization of valence

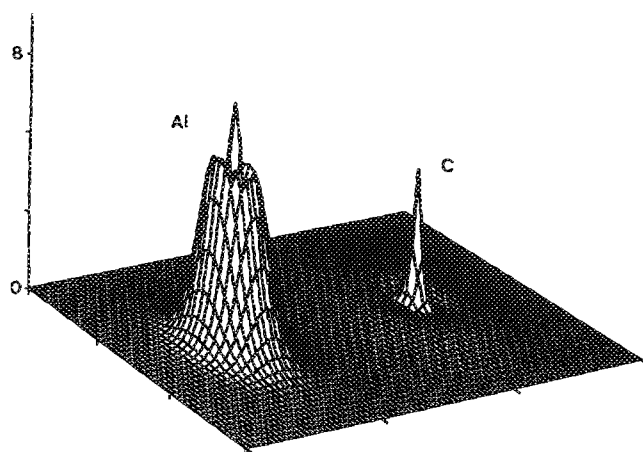


FIG. 1. Difference in the electronic charge density between the self-consistent and superimposed free atom values in AlC. The values at the Al site have been truncated at 8.0 to show details.

levels as well as by charge transfer from one level to another. The former dominates if the valence levels of the two atoms involved in the bonding are at nearly equal energies while the latter dominates if the levels are far apart. In Al and Si the hybridization plays a dominant role while in Al and C the charge transfer plays the major role in the bonding. The stronger binding between Al and C than that between Al and Si suggests that charge transfer is more dominant than the hybridization in strengthening the bond between the atoms.

One could also arrive at the same conclusion by looking into the ionization potentials of C, Al, and Si atoms which are, respectively, -11.26 , -5.99 , and -8.15 eV. Clearly, in the AlC dimer it would be energetically preferable to transfer electrons from Al to C, and not the other way around. Similar charge transfer can be predicted in

AlSi system. These predictions are verified in actual self-consistent calculations presented in Table II.

In conclusion, we have seen that the aggregation of Al to C-rich sites at Al-SiC interface as well as the core level shifts of Al and Si $2p$ levels could be understood qualitatively at a molecular level. We also show that atomic spectroscopy, in large part, could be used to understand the nature of the bonding and the charge transfers at the interface. For a quantitative understanding of the interfacial adhesion in metal-matrix composites it is, however, necessary to consider the geometry, composition, and atomic relaxations at the interface.

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