I. INTRODUCTION

Understanding the chemical bonding between Al and Si is of both fundamental and technological importance. Although Al and Si are neighbors in the periodic table, they exhibit rather different characteristics of bonding. Bulk aluminum is an excellent metal while bulk silicon is a covalently bonded semiconductor. The bonding between Al and Si is expected to show both ionic and covalent characters. Technologically, aluminum thin films are widely used in Si-based microelectronic devices as electrical contacts and conductors. The interactions between Al and Si play important roles in determining the nature and quality of the Al/Si interface. Extensive work has been conducted on the deposition and growth of Al thin films on Si and SiO2 surfaces.1–3

Studying AlSi mixed clusters can provide knowledge about the nature of the Al/Si chemical bonding, as well as insight into the properties of the Al/Si interfaces important to the current electronic devices. Surprisingly, there has been no work on the AlSi mixed clusters, although there have been numerous studies on pure Al4–9 and Si clusters.10–11 Part of the difficulty in studying the AlSi clusters is their production and mass analyses. Al and Si have very close atomic masses and good mass resolution will be required to analyze the AlSi clusters, which may show complicated mass patterns.

We are interested in studying the electronic structure of the AlSi clusters by using anion photoelectron spectroscopy (PES). In the present paper, we first report the results on the simplest of the AlSi mixed clusters, the AlSi mixed dimer. We obtained vibrationally resolved PES spectra for AlSi− at 2.33 and 3.49 eV photon energies. We observed four electronic excited states for AlSi− within about 1.1 eV above the ground state. For comparison, we also studied the PES spectra of Al2− at 2.33, 3.49, and 4.66 eV photon energies. Beside the neutral states, we observed two electronically excited states for the Al2− anion. Interestingly we found that the electron affinity (EA) of AlSi− (1.32 eV) is smaller than that of both Al2− (1.46 eV) and Si2− (2.20 eV, Ref. 14). The results of the Al2− are compared with previous theoretical calculations.3 We discuss the bonding and electronic structures of AlSi by comparison with Al2 and Si2 since there has been no theoretical calculation on the AlSi dimer.

II. EXPERIMENT

The details of our experimental apparatus have been published before.15,16 Briefly, it involves a pulsed laser vaporization cluster source and magnetic-bottle time-of-flight photoelectron analyzer. A Si/Al alloy disk target (4:1 atomic ratio) is vaporized by a Q-switched Nd:YAG laser to produce the AlSi clusters. The clusters are entrained into a helium carrier gas and expanded through a 2 mm diameter nozzle to form a supersonic cluster beam. The anions in the beam are extracted perpendicularly into a time-of-flight (TOF) mass spectrometer for size analysis. In the dimer region, all the dimers, including Al2−, AlSi−, and Si2−, are produced in about equal abundance and they are separated by one atomic mass unit. Since Al has only one natural isotope (100% 27Al), the main AlSi− mass peak (27Al28Si) contains no other species while the main Si2− peak contains about 5% AlSi− (27Al29Si) due to the natural isotope distributions of Si (92.23% 28Si, 4.67% 29Si, 3.10% 30Si). During the PES experiments, a cluster of interest is mass selected and decelerated before detached in the interaction zone of the magnetic bottle by a laser beam from a second Nd:YAG laser. The photoelectrons are collected by the magnetic bottle at near 100% efficiency and energy analyzed in a 3.5 m long field-free TOF tube at a resolution of better than 30 meV for 1 eV electrons. The photoelectron TOF spectra are calibrated by the known spectrum of Cu2− to obtain the binding energy spectra usually presented.16

III. RESULTS

Figure 1 shows the 355 nm (3.49 eV) spectrum of AlSi− compared to that of Al2−. Five features are observed for AlSi,
labeled as X, A, B, C, and D. The feature A is very weak and the feature B is shown as a shoulder on the feature C. The 355 nm spectrum of Al$_2^-$ shows a strong and partially vibrationally resolved feature near 1.6 eV, which actually contains transitions to two electronic states of Al$_2$ (X and A, see below). There are also two weak features in the Al$_2^-$ spectrum, labeled as a and B, although the count rate and statistics for the feature B are poor.

The 532 nm spectrum of Al$_2$ and AlSi$_2$ are shown in Fig. 2. The spectra are better resolved at the lower photon energy. The X, A, and B features for AlSi are clearly vibrationally resolved. The 532 nm spectrum of Al$_2$ is only slightly better resolved, but several weak features, labeled as a’, b, and c, are clearly observed. We also obtained PES spectra for Al$_2^-$ and AlSi$_2^-$ at 266 nm (4.66 eV). Figure 3 shows the 266 nm spectrum of Al$_2^-$, compared with the two spectra at lower photon energies. It is seen that the feature B is observed much more clearly in the 266 nm spectrum. However, we did not observe any new features for the 266 nm spectrum of AlSi$_2^-$. All the observed binding energies and spectroscopic constants for Al$_2^-$ and Al$_2$, and AlSi are listed in the Tables I and II, respectively. The detailed assignments and discussion will be given in the following.

IV. DISCUSSION

A. Al$_2$ and Al$_2^-$

Before discussing AlSi, we first discuss Al$_2$ and Al$_2^-$ which are better understood. The spectroscopy and electronic structure of Al$_2$ have been extensively investigated.$^{3-7}$ Its electronic structure can be understood from the simple molecular orbital (MO) picture depicted in Fig. 4. The Al atom has a 3$s^2$3$p^1$ ($^2P$) ground state configuration. In the Al$_2$ dimer, the 3$s$ orbitals combine to form the 1$s_g$ and 1$s_u$ MOs which are fully occupied. The 3$p$ orbitals combine to form the 2$s_g$ and 1$\pi_u$ bonding MOs and the 1$\pi_g$ and 2$s_u$ antibonding MOs. Depending on the spacing between the
2\(\sigma_u\) and 1\(\pi_u\) MOs, there are three ways to fill the two electrons; 2\(\sigma_u^2\)\((3\Sigma_g^-\), 1\(\pi_u^2\)\((3\Sigma_g^+\), and 2\(\sigma_u\)1\(\pi_u\)\((1\Pi_u\)). Theoretical calculations predicted that the ground state of Al\(_2\) is the \(3\Pi_u\) state with a nearly degenerate \(3\Sigma_g^+\) state. Although there has been no direct experimental measurement on the \(3\Pi_u\)–\(\Sigma_g^-\) splitting, Sunil and Jordan predicted this splitting to be within 200 cm\(^{-1}\) and Bauschlicher et al.’s best estimate is 174 cm\(^{-1}\).6 The \(1\Sigma_g^-\) state is calculated to lie at least 2000 cm\(^{-1}\) higher in energy. Sunil and Jordan also calculated the various anion states of Al\(_2\). In anion ground state, the extra electron enters the 1\(\sigma_u\) MO to give a \(4\Sigma_g^-\) (2\(\sigma_u\)1\(\pi_u\)) state.3

The PES spectra of Al\(_2^+\) can be assigned easily using the known information about Al\(_2\) and Al\(_2^-\). Detachment of a 1\(\sigma_u\) electron from Al\(_2^-\) yields the X \(3\Pi_u\)\((2\sigma_u^2\pi_u^6\)) ground state while removal of the 2\(\sigma_u\) electron gives the \(A\ 3\Sigma_g^+\) (1\(\pi_u^6\)) excited state. We assign the main features of the PES spectra of Al\(_2^+\) near 1.6 eV to these two transitions, as shown in Figs. 1 and 2. Unfortunately, these two states cannot be clearly resolved in the current experiment due to the small spacing between the two states. The partially resolved vibrational structure gives an average spacing of about 320 cm\(^{-1}\), which is between the vibrational frequencies of the X \(3\Pi_u\) (285.8 cm\(^{-1}\)) and \(A\ 3\Sigma_g^+\) (350.0 cm\(^{-1}\)) states (see Table I). At 532 nm, the spectrum of Al\(_2^+\) (Fig. 2) is only slightly better resolved than the 355 nm spectrum (Fig. 1), even though the spectral resolution was better at the low photon energy. This is consistent with the fact of two overlapping states. The 532 nm spectrum also shows an unusual Franck–Condon envelope. This suggests that probably the relative cross sections of the two states are photon-energy dependent. The hot band transitions (features b and c) also seem to be more significant in the 532 nm spectrum.

Besides the X \(3\Pi_u\) and \(A\ 3\Sigma_g^+\) states, detachment from the 1\(\sigma_u\) and 2\(\sigma_u\) MOs of Al\(_2^-\) can also produce singlet states: \(1\Pi_u\)\((2\sigma_u^2\pi_u^6\)), \(1\Delta_g\)\((1\pi_u^6\)), and \(1\Sigma_g^+\)\((1\pi_u^6\)). These excited states of Al\(_2^+\) neutral were predicted to be all within 1 eV of the ground state.6 However, none of these states is observed in the PES spectra within about 1.5 eV above the ground state, as shown in Fig. 3, where the spectra at three photon energies are compared. A broad band, labeled as B, is observed near about 3.1 eV (1.6 eV above the ground state). This feature was assigned to be from detachment of a 1\(\sigma_u\) electron \(\left(5\Sigma_u^-\right.,1\sigma_u^2\left(\sigma_u^2\pi_u^2\right.,\ 2\pi_u\))\ Fig. 4\) by Cha et al. in a previous PES study of Al\(_2^-\) clusters, on the basis of their resolved vibrational frequency (\(~\sim450\) cm\(^{-1}\)).9 We did not vibrationally resolve this band due to the low count rate in the 355 nm and the poor deceleration of the Al\(_2^-\) anion in the 266 nm spectrum. Since the excitation energy (\(~\sim1.6\) eV) of the B feature is significantly higher than any of the calculated singlet states, its assignment to the \(5\Sigma_u^-\) state seems reasonable. However, we cannot explain why none of the singlet states is observed for the Al\(_2\) dimer since we have shown that such low spin states are easily observed in PES.

### Table I. Observed binding energies (BE) and spectroscopic constants for \(\text{Al}_2\) and \(\text{Al}_2^-\) compared to literature values.

<table>
<thead>
<tr>
<th></th>
<th>BE (eV)</th>
<th>Term value (eV)</th>
<th>Vib. freq. (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{Al}_2)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(X\ 4\Sigma_g^-)((\sigma_u^2\pi_u^6))</td>
<td>1.32(4)(*)</td>
<td>0</td>
<td>400(50)</td>
</tr>
<tr>
<td>(A\ 3\Sigma_g^-)((\sigma_u^2\pi_u^6))</td>
<td>1.55(4)</td>
<td>0.23(4)</td>
<td>400(80)</td>
</tr>
<tr>
<td>(B\ 2\Delta_l)((\sigma_u^2\pi_u^6))</td>
<td>1.99(4)</td>
<td>0.67(4)</td>
<td>400(60)</td>
</tr>
<tr>
<td>(C\ 2\Pi_l)((\sigma_u^2\pi_u^6))</td>
<td>2.14(4)</td>
<td>0.82(4)</td>
<td>400(80)</td>
</tr>
<tr>
<td>(D\ 2\Sigma_g^-)((\sigma_u^2\pi_u^6))</td>
<td>2.45(S)</td>
<td>1.13(4)</td>
<td>400(80)</td>
</tr>
</tbody>
</table>

\(*\)The measured adiabatic electron affinity of Al\(_2^-\).

### Table II. Observed binding energies (BE) and spectroscopic constants for \(\text{AlSi}\) dimer.

<table>
<thead>
<tr>
<th></th>
<th>BE (eV)</th>
<th>Term value (eV)</th>
<th>Vib. freq. (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(X\ 4\Sigma_g^-)((\sigma_u^2\pi_u^6))</td>
<td>1.32(4)(*)</td>
<td>0</td>
<td>400(50)</td>
</tr>
<tr>
<td>(A\ 3\Sigma_g^-)((\sigma_u^2\pi_u^6))</td>
<td>1.55(4)</td>
<td>0.23(4)</td>
<td>400(80)</td>
</tr>
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<td>(B\ 2\Delta_l)((\sigma_u^2\pi_u^6))</td>
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<td>1.13(4)</td>
<td>400(80)</td>
</tr>
</tbody>
</table>

\(*\)The measured adiabatic electron affinity of Al\(_2^-\).
experiments of many open shell dimers, including AlSi (see below) and Si$_2$.

The low binding energy features (a’, a, b, and c, Fig. 2) that are more prominent in the 532 nm spectrum seem to depend on source conditions and are likely due to hot bands or excited states of the Al$_2^-$ anions. The a’ and a features are present in all the spectra in Fig. 3 while the b and c features are more prominent in the 532 nm spectrum. We assign the b and c features to be hot band transitions. The a’ and a features should be due to electronically excited states of the Al$_2^-$ anion.

Sunil and Jordan have extensively calculated the anion excited states and found five such states. The Al$_2^-$ ground-state configuration, 2σ$^1_g$ 1π$^0_u$, can result in four electronic states; 4Σ$^-$, 2Σ$^-$, 2Δ$^-$, and 2Σ$^+$, where the 4Σ$^-$ is the ground state. There are also two 2Π$^u$ states resulting from the following configurations: 1π$^0_u$ and 2σ$^1_g$ 1π$^0_u$. All of these five excited states were calculated by Sunil and Jordan and were found to be bound in their configuration-interaction (CI) calculations. They also calculated the adiabatic detachment energy for the 4Σ$^-$ ground state (EA of Al$_2$) and the two 2Π$^u$ states using the coupled-cluster doubles+single and triple excitations (CCD+ST) methods, which gave more accurate energies. The latter results are listed in Table I and compared with the current measured values. The agreement is excellent, particularly for the EA, upon which the calculated value is well within the experimental uncertainty. Therefore, it seems reasonable to assign the two observed excited states of Al$_2^-$ (a and a’) to the two 2Π$^u$ states, respectively.

B. AlSi

The electronic structure of the AlSi dimer may be understood by comparing with that of Al$_2^-$ to which it is isoelectronic. The AlSi$^-$ is isoelectronic to Si$_2$, which is also well understood. Due to the difference of the ionization potentials of Al (5.98 eV) and Si (8.15 eV), the Al–Si chemical bonding is expected to exhibit both ionic and covalent characters with some degree of charge transfer from Al to Si.

Figure 4 shows a schematic MO diagram of AlSi, compared to that of Al$_2$. The 3σ and 1π orbitals are the bonding MOs between the 3p orbitals of Al and Si. AlSi has one more electron than Al$_2$, and again there are three ways to fill the three 3p-type electrons depending on the 3σ and 1π orbital separation: 3σ$^1$ 1π$^2$, 3σ$^2$ 1π$^1$, 3σ$^0$ 1π$^3$. Since Al$_2$ has a 2σ$^1_g$ 1π$^0_u$ ground-state configuration, we think that AlSi most likely has a similar configuration, giving a 4Σ$^-$ (3σ$^1$ 1π$^2$) ground state for AlSi. Analogously, it would be reasonable to assume that the AlSi$^-$ ion should have a similar configuration as the isoelectronic Si$_2$ dimer, i.e., a 3Σ$^-$ (3σ$^2$ 1π$^2$) ground state. Based on this ground-state configuration of AlSi$^-$, the following detachment channels can be expected by removing electrons from the 3σ and 1π orbitals:

$$3σ^1 1π^2 → 3σ^1 1π^2, \quad 4Σ^-, 2Σ^-, 2Δ, 2Σ^+$$  \hspace{1cm} (1)

$$→ 3σ^2 1π^1, \quad 2Π^u$$ \hspace{1cm} (2)

where the 4Σ$^-$ state represents the ground state of AlSi, and all the other states are the excited states of AlSi. The detachment from the 3σ-type 2σ orbital is expected to have much higher energy and is probably not accessible at the photon energies used presently.

According to Eqs. (1) and (2) above, we expect to observe five detachment channels. These are indeed born out from our observation of the five features in the photoelectron spectrum, as shown in Fig. 1. The ground state feature (X) corresponds to the 4Σ$^-$ state. The C feature is quite strong and its intensity seems to increase at the higher photon energy, as seen from Figs. 1 and 2. Since detachment cross section is expected to increase with photon energies for electrons with higher angular momenta, we assign the feature C to the 2Π state, as a result of removing a 1π electron. The A, B, and D features are relatively weak and they are likely to be due to the doublet states derived from the 3σ$^1$ 1π$^2$ configuration, as shown above.

AlSi is isoelectronic to Al$_2^-$ whose electronic states have been calculated by Sunil and Jordan, as mentioned above. The ordering of the doublet states derived from the 2σ$^1_g$ 1π$^0_u$ configuration of Al$_2$ at the CI level of calculations is 3Σ$^-$, 2Δ$^-$, 2Σ$^-$, 2Σ$^+$, 2Σ$^+$. Therefore, we assign the A, B, and D features to the 3Σ$^-$, 2Δ, 2Σ$^+$ states, respectively, as shown in Table II.

All the three doublet states show a vibrational progression, similar to the ground state, consistent with the fact that they all derive from the same electron configuration. The 2Π(3σ$^2$ 1π$^1$) state (feature C) shows one single peak with little vibrational excitation, suggesting that the 1π orbital is rather nonbonding in AlSi. Our assignment and the observed spectroscopic constants for all the states for AlSi are summarized in Table II. Figure 5 shows pictorially the energy levels of the AlSi dimer and the detachment transitions from the AlSi$^-$ ion. It is interesting to point out that the 2Π(2σ$^1_g$ 1π$^0_u$) state in Al$_2^-$ is between the 2Δ$^-$ and 2Σ$^+$ states in Sunil and Jordan’s calculations. This is also consistent with our spectral assignment for AlSi. Nevertheless, our assignments should be considered tentative, largely based on the known information about Al$_2^-$ and Si$_2$. Accurate ab initio theoretical calculations on this simple heterodimer are indeed called for in light of the current spectroscopic and electronic energy level information.

C. Comparison of the electronic structures of Al$_2^-$, AlSi, and Si$_2$

The Al$_2^-$, AlSi, and Si$_2$ dimers form an interesting series of electronic systems, each with an additional electron. AlSi is expected to show properties between Al$_2$ and Si$_2$, as well as different properties due to the heterobonding. All three dimers are open shell electronic systems and all possess rich low-lying electronic states. These low-lying electronic states are easily observed for the AlSi and Si$_2$ dimers in their anion photoelectron spectra. However, these states are not observed in the Al$_2^-$ photoelectron spectra, even though such states have been calculated to exist within the energy range accessible at our photon energies. The vibrational frequency for the ground state of AlSi is 400 cm$^{-1}$, which is almost
exactly the average of the ground-state vibrational frequencies of $\text{Al}_2$ (285.8 cm$^{-1}$) and $\text{Si}_2$ (509 cm$^{-1}$). This suggests that the bonding energy of $\text{AlSi}$ is probably also between that of $\text{Al}_2$ and $\text{Si}_2$. The $\text{Si}_2$ has a much higher EA than $\text{Al}_2$. We expected that the EA of $\text{AlSi}$ would be between the values of $\text{Al}_2$ (1.46 eV) and $\text{Si}_2$ (2.20 eV). Surprisingly, our observed EA for $\text{AlSi}$ (1.32 eV) is smaller than that of both $\text{Al}_2$ and $\text{Si}_2$.

It is interesting to compare the energy separation between the $\sigma_{3p}$ and $\pi_{3p}$ orbitals among the three molecules. As shown in Fig. 6 (upper) schematically, both $\text{Al}_2$ and $\text{Si}_2$ have an excited state very close to the ground state, involving the transfer of an electron from the $\pi_g(3p)$ to the $\pi_u(3p)$ orbitals. This suggests that the $\sigma_g(3p)$ and $\pi_u(3p)$ orbitals are nearly degenerate in these two homonuclear molecules. The $\text{AlSi}$ heterodimer is different from $\text{Al}_2$ and $\text{Si}_2$ in two respects. First, the electron transfer in $\text{AlSi}$ is from the $\pi_u(3p)$ to $\pi_g(3p)$; and second, the energy separation is much larger in $\text{AlSi}$ (Fig. 6, upper). This implies that the $\pi$ orbital is more stable in $\text{AlSi}$ than that in $\text{Al}_2$ and $\text{Si}_2$. Schematic MO diagrams depicting the $3p-3p$ interactions for the three molecules are compared in Fig. 6 (lower). The heteronature of bonding between $\text{Al}$ and $\text{Si}$ is shown clearly. The stabilization of the $1\pi$ orbital in $\text{AlSi}$ indicates that it probably has more $\text{Si}$ character. Similarly, the $3\sigma$ orbital is probably of more $\text{Al} 3\pi$ character, naturally explaining the lower EA of the $\text{AlSi}$ heterodimer, because the $\text{Al}$ atom itself has a very small EA (0.441 eV, Ref. 19).

The near degeneracy of the $2\sigma_g$ and $1\pi_u$ orbitals causes the existence of low-lying excited states for the $\text{Al}_2^-$ and $\text{Si}_2^-$ anions. Such low-lying excited states for the $\text{AlSi}^-$ anion are not observed, consistent with the simple MO picture presented here.

V. CONCLUSIONS

We report the first study of the $\text{AlSi}$ heterodimer using anion photoelectron spectroscopy. Four low-lying excited states are observed for $\text{AlSi}$. The electronic structure of $\text{AlSi}$ is understood by comparing with that of the well-studied $\text{Al}_2$ and $\text{Si}_2$ dimers. We find that the EA of $\text{AlSi}$ is surprisingly lower than that of both $\text{Al}_2$ and $\text{Si}_2$ although the ground-state vibrational frequency of $\text{AlSi}$ is found to be nearly the average of that of $\text{Al}_2$ and $\text{Si}_2$. This is explained based on the heteronature of the molecular interactions between the $\text{Al} 2p$ and $\text{Si} 3p$ orbitals. We also present the photoelectron spectra of $\text{Al}_2^-$ and the definitive observation of low-lying excited states for the $\text{Al}_2^-$ anions, which are compared to existing $ab\ initio$ calculations. Theoretical studies on the simple $\text{AlSi}$ heterodimer would be interesting to confirm the current assignments and interpretation.

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