Electronic states of two-dimensional adatom gas and nanocluster array: Na on Si(111)7×7

J. R. Ahn, K. Yoo, J. T. Seo, J. H. Byun, and H. W. Yeom*
Institute of Physics and Applied Physics and Center for Atomic Wires and Layers, Yonsei University, Seoul 120-749, Korea
(Received 2 June 2005; revised manuscript received 29 July 2005; published 15 September 2005)

Electronic structure evolution of Na adsorbates on Si(111)7×7 has been investigated by angle-resolved photoemission spectroscopy, which was recently reported to transit from a two-dimensional adatom gas state to a nanocluster array as Na coverage increases [Wu et al., Phys. Rev. Lett. 91, 126101 (2003)]. The distinct electronic states being characteristic to the adatom gas and the nanoclusters are clearly resolved. Both phases are semiconducting and the nanocluster-induced state has a higher binding energy than that due to the mobile adatoms. The adatom-induced state shifts systematically to a higher binding energy as the density of the adatoms increases in the gas phase. This is apparently incompatible with the localized bond formation between an adatom and Si atom(s). The effective delocalization of the bond charge through the dynamic motion of adatoms is proposed.

DOI: 10.1103/PhysRevB.72.113309

In close relation to their fundamental quantum properties, nanoclusters are important as potential candidates of high-density recorders, light-emitting sources in the nanoscale optoelectronics, nanoscale catalysts, and toolkits in biomolecular synthesis. A well-ordered array of nanoclusters with an identical size is essential for many such applications but difficult to be realized. The spontaneous self-assembly on solid surfaces is one of the successful ways to produce such nanoclusters massively and uniformly. The recent examples include Cu on Pt(111), group-III metals (Al and In) on Si(001), Fe on Cu(111), and Pd on SrTiO3(001). However, the size distribution, the lateral ordering, and the stability of these systems are seldom satisfactory.

In this respect, the metal nanoclusters on Si(111)7×7 have drawn particular interest. A wide range of metals (In, Pb, Na, Ga, and Mn) was found to form nanocluster arrays on the 7×7 mesh of the Si(111) substrate [Fig. 1(b)] with an identical (“magic”) size and, thus, the size distribution and the lateral ordering are close to perfection. Moreover, these magic nanoclusters are stable above room temperature in contrast with most of the metal nanoclusters on metal surfaces. Similar degrees of the ordering and the stability could also be observed on the In-induced nanocluster array on Si(001). A number of studies have been performed for the growth behaviors and the atomic structures of the magic clusters on Si(111), which suggested an essentially common registry of a cluster with six metal and three Si atoms with possibly different bond networks depending on the adsorbate metals [see Fig. 1(b)].

Among the magic nanoclusters on Si(111)7×7, the growth mechanism of Na nanoclusters was recently reported to be unique. That is, Na nanoclusters are formed only above a critical coverage of 0.08 monolayer (ML), and below this coverage the adatoms are highly mobile, hopping between the stable (“basin”) sites [see Fig. 1(a)] to constitute a two dimensional (2D) gaslike phase. This 2D gas-solid transition is also important electronically since it was suggested as the atomistic origin of the abrupt work function change of the surface, a long standing issue. However, no detailed electronic structure study for Na (or even other metals) adatoms and nanoclusters on Si(111)7×7 has been available. Such an electronic structure study would be crucial also for the understanding of the intriguing bonding nature of monovalent noble metal atoms on Si(111)7×7 as discussed very recently.

In this Brief Report, we report on the angle-resolved photoemission (ARP) study of the Na adatoms and nanoclusters on Si(111)7×7. The characteristic electronic states of the

FIG. 1. (Color online) (a) Possible Na adsorption sites on Si(111)7×7, indicated by numbers from 1 to 9. (b) Atomic structure model of the Na nanocluster with ΘNa of 0.12 ML, where the yellow-filled sphere denotes a Na adsorbate. (c) Change of a work function (Δϕ) as increasing ΘNa, measured from photoelectron spectra.
2D gas (mobile adatoms) and solid (magic nanocluster array) phases were identified clearly as well as their evolution through the phase transition. For the case of the gas-like adatoms, an unusual progressive shift of the binding energy of the corresponding electronic state was observed. This is not consistent with the formation of usual localized bonds between the adatoms and substrate Si atoms but may be explained by the electron delocalization due to the highly dynamic motion of adatoms. The magic nanoclusters were found to be insulating with two characteristic energy states at binding energies of 0.4 and 1.2 eV, which provides important insights and questions into the structure model.

The ARP measurements were performed using a high-resolution angle-resolved electron analyzer (SES-100, Gamma Data) and He I radiation (hν=21.2 eV) at a base pressure of 4×10⁻¹¹ Torr. The nominal energy and angular resolution was better than 13 meV and 0.2°, respectively. Na atoms were deposited using a well-degassed Na dispenser onto a well-cleaned Si$_{111}$ substrate held at room temperature. The evaporation rate was fixed at 0.022 ML/min in order to maintain the growth conditions as close as the previous scanning tunneling microscopy (STM) experiment. The relative Na coverage ($\Theta_{Na}$) was calibrated from the well-established work function changes as measured from the secondary electron cutoff in the normal-emission ARP spectra.

Figure 1(c) shows the well-known change of the work function as increasing $\Theta_{Na}$ at room temperature. At this coverage range, there are two abrupt breaks in the rate of the work function change, defining three distinctive regions in the coverage (denoted as Phases I, II, and III, respectively, in the figure). It is rather straightforward to expect different adsorption behaviors, structurally and/or electronically, for those coverage ranges. While the atomistic details of such abrupt changes in adsorption behaviors had been uncertain for a long time, the recent STM study indicated that the Phases I, II, and III, respectively, correspond to the highly mobile adatom gas phase, the magic nanocluster array, and the decay of the nanoclusters.

Figure 2 shows the ARP spectra close to the Fermi level around the Si bulk band-gap region for increasing Na coverage from 0.005 to 0.50 ML. The ARP spectra of alkali metals on the clean Si$_{111}$ surface were measured previously, but the spectral changes at low coverage were not detailed. The spectra shown in the figure were taken at an emission angle of 12° from the surface normal, where all the surface states S1, S2, and S3 of the clean Si$_{111}$ surface are observed clearly. The surface states S1–S3, with binding energies of 0.16, 0.84, and 1.70 eV, respectively, have been known to originate from Si adatoms, restatoms, and back-bonds of adatoms, respectively. Adatoms located near the corner holes (so-called “corner adatoms”) were reported to produce another surface state S1' at a binding energy of 0.5 eV, which is, however, not clearly resolved at this emission angle.

For the initial adsorption of Na, the decay of the rest-atom state S2 is conspicuous. In addition, from about $\Theta_{Na}$=0.015 ML, a new state N1 develops at a similar binding energy...
with the adatom state S1. N1 grows in intensity, which is
accompanied by the gradual decrease of the intensity of S1
(and also S3). In order to analyze the spectral changes more
quantitatively, the ARP spectra were fitted by Gaussian
curves and polynomial backgrounds (the inset of Fig. 3). As
shown in Fig. 3(b), N1 is enhanced gradually, reaches a
maximum intensity at about 0.04 ML, and fades at higher
\( \Theta_{Na} \) to disappear at \( \sim 0.12 \) ML. It is noted that the binding
energy of N1 increases along with \( \Theta_{Na} \) from a smaller value
than 0.36 up to 0.56 eV, while S1–S3 keep nearly the same
binding energies. This is important as discussed further below.

In contrast to the initial spectral changes discussed above,
at \( \Theta_{Na} \gtrsim 0.12 \) ML, two new spectral features, N2 and N3, are
observed at binding energies of 0.5 and 1.1 eV, respectively.
The intensities of both N2 and N3 are maximized at \( \sim 0.22 \) ML,
where the density of the Na-induced nanoclusters was
reported to reach a maximum. At a higher \( \Theta_{Na} \), N2 and N3
disappear and yet another state N4 develops with a higher
binding energy of 1.4 eV.

As shown above, the spectral evolution of the surface
upon Na adsorption can obviously be divided into three
different regions of coverages, as bounded roughly at
\( \Theta_{Na} \sim 0.11 \pm 0.03 \) and 0.25±0.05 ML. These coverages are
estimated from the crossovers of the intensities of the char-
acteristic and well-resolved spectral features of each region,
N1, N2/N3, and N4, respectively. These three different re-
gions as defined by the ARP spectral evolution correspond
well with Phases I, II, and III, which are identified by the
work function and the structural changes.\(^{11}\) Therefore, we
can unambiguously conclude that the N1, N2/N3, and N4
states, respectively, represent the mobile Na adatoms (Phase
I), the Na nanoclusters (II), and the higher coverage phase
(III) with an uncertain structure. In fact, the phase boundaries
determined by the work-function change are 0.88 and 0.22
ML, which correspond to the coverages where the nanoclus-
ters start to form and to decay according to the previous
STM study.\(^{11}\) If we apply this strictly to the spectral behav-
iors, the phase boundaries should corresponds the coverages
where the N1 and N3 (N2) states start to decay, respectively,
that is, 0.88 and 0.22 ML in better agreement with the work-
function data. With a proper theoretical calculation, the N1,
N2/N3, and N4 states, more exactly their binding energies,
can be used as a good touchstone of the available structure
models of each phase. However, even before the quantitative
comparison, the characteristic spectral features and their evo-
lutions provide important qualitative insights as discussed
below.

In the adatom gas phase (Phase I), an adatom is adsorbed
on the hollow sites around a Si restatom [the so-called basin
sites; Sites 3, 4, 5, and 9 along the rings in Fig. 1(a)]. The
diffusion barriers within the basin, between the basins within
a half unit cell, and between the half unit cells, were calcu-
lated to be 140, 360, and 420 meV, respectively.\(^{16}\) This
indicates that the mobility of adatoms is very high at
room temperature with the corresponding hopping rates of
\( 7 \times 10^{10}, 1 \times 10^{9}, \) and \( 1 \times 10^{8} \) hop/s. Note that two adatoms
within a basin are repulsive and, thus, the adatoms are in a
2D lattice gas phase with a triangular lattice of basins. This
phase was reported to persist only up to 0.08 ML (four Na
adatoms among six available basins in a \( 7 \times 7 \) unit cell) by
the STM experiment and the theoretical calculation.\(^{11}\) How-
ever, the bonding nature between the adatoms and the Si
surface atoms (the restatoms and the adatoms) is not obvious
enough. That is, although the low-coverages alkali-metal ad-
sorbates on Si surfaces are generally believed to be ionic,\(^{1,13}\) it
is not clear how the transferred charge is distributed into the
Si surface atoms. This problem becomes more tricky since
the stable adsorption site is not a highly symmetric site, such
as that on top of adatoms or restatoms. This peculiar bonding
situation was pointed out very recently for monovalent Ag,
Au, and Cu adsorbates.\(^{1,13,18}\)

In the present experiment, it is shown that the Na initial
adatoms affect both adatoms (S1) and restatoms (S2). This
indicates that the transferred electrons from Na are not local-
ized on adatom nor restatom dangling bonds. This seems
consistent with the basin site model, where the adatoms are
mobile in the middle of three adatoms and one restatom. The
transferred electrons yield a new well-defined surface state
N1. What is more important is that the the binding energy of
N1 increases systematically as \( \Theta_{Na} \) increases. This binding
energy shift is obviously not compatible with the localized
ionic (or partially covalent) bond formation between the ad-
sorbate and Si atoms. This is because such localized bonds
cannot be affected significantly by the adsorbate coverage.
Instead, the straightforward picture is that the binding energy
is fixed while the intensity of the corresponding spectral fea-
ture increases with respect to the adsorbate density. The pos-
sible band bending shift, as widely observed in the low cov-
erage alkali metal adsorption,\(^{14,15}\) was corrected already by
aligning the spectra with the well-defined Si bulk spectral
feature. This correction is further corroborated by the nearly
constant binding energies of other spectral features, such as
S1–S3. One can also think of a gradual change of the adsorp-
tion structure, which is, however, not justified by the recent
theoretical calculation.\(^{11,16}\) Note that such a change of ad-
sorption structure, if any, would induce not a gradual evolu-
tion of the binding energy but a discrete change of the spec-
tral features as in the case from N1 to N2/N3.

A reasonable explanation of the binding energy shift of
N1 may be the delocalization of the transferred electrons on
the surface, which makes the density of adatoms systemati-
cally affect the binding energy. However, the electron delo-
calization of the N1 state (and also N2–N4) is not easily
conceived since it has almost no noticeable dispersion as
other surface states of Si(111)7×7.\(^{17}\) Based on the above
considerations and constraints, we suggest that the trans-
ferred electrons might be delocalized by the highly dynamic
adsorbate motion (hopping). That is, the hopping adsorbate
could not be in the ionic state but carry the electrons to be
transferred into the next site. This means that if we have only
one Na adatom within a half unit cell then effectively one-
sixth of the total transferred charge from Na is donated into
each Si adatom in time average. Then, the effective trans-
ferred charge from Na adatoms into one Si adatom, would be
proportional to (or at least dependent on) \( \Theta_{Na} \) until Na atoms
occupy all the available sites. In this case, the hopping rate
is expected to be faster than the photoemission time scale
(\( \sim \) ps). However the present theoretical values mentioned
above are much slower.\(^{11}\) Thus, the delocalization by dy-
namic adatom motion is not conclusive yet and the exact mechanism of the delocalization of the bond charge needs to be investigated further.

Above $\Theta_{Na}$ of 0.08 ML, the mobile Na adatoms were reported to freeze into nanoclusters with a structure of Fig. 1(b).\textsuperscript{11} The corresponding electronic states and the clusterization transition are well resolved in this experiment by N2 and N3. From its binding energy and intensity, N3 is naturally assigned as due to the Na—Si bonding within the cluster. A higher binding energy of N3 than N1, then, can be related to the electronic energy gain of the cluster formation. The presence of N2 can also be understood qualitatively from the structure model. The binding energy of N2 is nearly the same as that of the Si corner adatoms of clean Si(111)7×7. This is consistent with the model since the nanoclusters do not disturb significantly the Si corner adatoms. That is, we suggest that the N2 state is the dangling bond state localized on the Si corner adatoms after the cluster formation.

Although the N2 and N3 states seem qualitatively consistent with the present structure model, it would be necessary to confirm its binding energies through an \textit{ab initio} band calculation. Moreover, there are still uncertain points in the electronic structure of the magic nanoclusters. According to the present model, the total number of electrons in the 7×7 unit cell is odd since six electrons are provided by six Na adsorbates, and the Si atoms in a 7×7 unit cell have an odd number of electrons. Then, the nanoclustered surface is expected to be metallic in the electron counting scheme. This is apparently not compatible with the present experiment showing an energy gap larger than 0.25 eV for the whole coverage range of the nanocluster phase (Phase II). Moreover, the detailed picture of the Na—Si bonding within the cluster is lacking. The adatom in a cluster sits on the site to saturate three Si dangling bonds (two from the Si underneath and one from the Si trimers in the center of the cluster), which seems natural for the group III or IV adsorbates (Pb and In)\textsuperscript{10,13} but not for the monovalent adsorbate of Na. These puzzles should be solved in the future work for a better understanding of the electronic and energetic properties of the magic nanoclusters on Si(111). The detailed comparison of the electronic states of the Na case with those of group-III or IV adsorbates would be interesting in this sense.\textsuperscript{19}

This work was supported by KOSEF of MOST through the Center for Atomic Wires and Layers of the CRi program.

\textsuperscript{a}Author to whom all correspondence should be addressed.

Electronic address: yeom@phya.yonsei.ac.kr


