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Vibrational properties of Na nanoclusters self-assembled on Si(1 1 1) surface

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ABSTRACT

We have investigated structural and vibrational properties of Na nanoclusters self-assembled on the Si(1 1 1)-7 × 7 surface at room temperature mainly using high-resolution electron-energy-loss spectroscopy. We observe three characteristic loss peaks L_1, L_2, and L_3 ascribed to an interband transition, a local atomic vibration, and another interband transition from an Na nanocluster-induced state, respectively. The spectral change of L_1 with Na coverage θ suggests that the S_1 dangling bond band is gradually filled up to open a band gap with increasing θ up to 1.1 eV when all three loss peaks completely disappeared. The relatively high loss energy $E_l = 243$ meV of L_2 with a narrow linewidth of 32 meV indicates the only Na–Si atomic vibrational mode with Na atoms occupying the tilted on-top sites above Si rest atoms. Furthermore the extremely weak loss peak L_3 visible at a coverage range unique only to the Na nanoclusters proves the presence of a Na nanoclusters-induced electronic state N_2. These observations provide explanation to most unresolved spectral behavior of earlier photoemission study and evidence for the atomic structure of the Na nanocluster.

Nanoclusters are attractive host for the diverse industrial applications including quantum information processing, optical devices, and biology due to their atomic like electronic properties [1–3]. Various experimental approaches such as lithography, etching, and a method using the periodicity of solid surfaces have been adopted to grow such nanoclusters [4–6]. Recently, several atomic species have been reported to form lattice-like arrays of nanoclusters self-assembled on the Si(1 1 1)-7 × 7 surface at room temperature [7,8,10,11,9].

As reported by Cho and Kaxiras, metal adsorbates occupy high symmetry sites around Si restatoms within the so-called attractive basins to form nanoclusters [12]. Since there are three attractive basins in each faulted half unit cell (FHUC) and unfaulted half unit cell (UHUC), nanoclusters in their stable configurations tend to make a lattice-like array as observed in scanning tunneling microscope (STM) images. Most nanoclusters formed on the Si(1 1 1)-7 × 7 surface are found to be semiconducting and contain six adsorbate atoms in each nanocluster [7,8,10,11,9]. One of the interesting features of such nanoclusters exhibiting atomically well resolved STM images is that most metal adsorbates cause significant rearrangement of the substrate Si atoms upon forming nanoclusters at room temperature (RT) [7,8] although some exceptions have also been reported [10,11,9].

Sodium (Na) nanoclusters, in particular, show some distinct features compared with other nanoclusters [7,13]. Wu et al. reported that there are three regions in the curve of work function change with increasing Na coverage θ revealing two inflection points at $\theta_1 = 0.08$ monolayers (MLs) and $\theta_2 = 0.22$ ML. For $\theta \leqslant 0.08$ ML, the surface shows a gas-like phase with atomically unresolved STM imgages where Na atoms appear to be quite mobile on the surface. For $0.08\ \text{ML} \leqslant \theta \leqslant 0.22$ ML, Na atoms form nanoclusters with a maximum density at 0.22 ML. Based on their STM observation and theoretical calculations, they proposed an atomic model where each Na nanocluster contains six Na atoms in the form of a triangle surrounding a Si trimer in the middle formed by Si adatoms moved inward (see Fig. 3 in Ref. [7]). Meanwhile Ahn et al. reported angle-resolved photoemission (ARP) study that new surface states associated with Na adsorption appear for each stage of adsorption, and demanded a theoretical calculation of band structure to explain spectral behaviors of these states [13].

With this background, we have investigated properties of electronic excitations associated with the formation of Na nanoclusters on the Si(1 1 1)-7 × 7 surface. We find three characteristic loss peaks in our high-resolution electron energy loss spectroscopy (HREELS) that behave quite differently with θ. The behavior of a peak L_1 of loss energy $E_l = 300$ meV apparently stemming from an interband transtion from S_1 state near Fermi level persists until the completion of the array of Na nanoclusters at θ_2. Meanwhile another loss peak L_2 of $E_l = 243$ meV changes sensitively with θ showing a quite narrow linewidth of 32 meV. We ascribe L_2 to the atomic vibration of Na atoms occupying the on-top sites above

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Si restatoms. Another loss peak L_3 appears to be quite weak and is ascribed to an interband transition from the Na nanoclusters-induced state N_2. The presence of these loss peaks and their spectral behaviors with θ explain qualitatively most of the unresolved spectral features in previous ARP study [13]. In addition, the only atomic vibrational mode L_2 observed in our EELS spectra confirms the atomic model proposed by Wu et al., and explains the rather quick disappearance of S_2 state in earlier ARP study.

Experiments have been performed in two separated ultra-high vacuum chambers of STM and HREELS equipped with typical surface diagnostic probes such as low energy electron diffraction (LEED) and X-ray photoemission spectroscopy (XPS). The base pressure of the chambers has been maintained below 1×10^{-10} mbar during the whole experimental process. The EELS has a Leybold-Heraeus ELS-22 spectrometer constituted with two 127° cylindrical deflectors for both monochromator and analyzer, which yields an optimum resolution of 7 meV and a half-acceptance angle of 2°. The XPS primarily used to measure work function change induced by Na adsorption utilizes a concentric hemisphere analyzer and an X-ray source of Mg Kα radiation. A Si(1 1 1) sample was prepared by cutting a n-doped Si wafer of a resistivity $\sim 2\Omega$ cm into a ribbon shape of dimensions $5 \times 30 \times 0.5$ mm^3. We have followed a well-known cleaning recipe of the sample until we observe a well-defined 7×7 LEED pattern with a dark background showing no detectable impurity peaks (O 1s, C 1s) in XPS scan [14]. We have used a commercial Na SAES getter source to deposit Na atoms onto the clean Si(1 1 1)-7×7 surface. The Na deposition has been made at a deposition rate of 0.018 ML/min after 5 min cooling from annealing at 800 °C to ensure the adsorption of Na atoms at RT. The Na coverage has been calibrated by measuring work function change. All EELS measurements have been performed within one hour after cleaning the sample to avoid any contamination effect.

As shown in Fig. 1, we have also observed three different phases of Na nanoclusters upon forming on the Si(1 1 1)-7×7 surface at RT as reported by Wu et al. [7]. The sparse distribution of Na nanoclusters at $\theta \leqslant \theta_1$ is seen in Fig. 1a with most Na nanoclusters occupying FHUCs. With increasing θ, we find a lattice-like array of nanoclusters at θ_2 (Fig. 1c). With further deposition of Na, the nanoclusters appear to decay into a nonuniform distribution of clusters with deformed shapes (Fig. 1d). Our work function change versus θ curve ($\Delta\phi$) shown in Fig. 2 also exhibits two infection points at θ_1 and θ_2 as observed by Wu et al. [7]. The three different stages I, II, and III as distinguished by different slopes and also different STM images in Fig. 1 illustrate the different phases of forming nanoclusters. The stage I identified as a gas-like phase reveals a rapid linear drop of work function as mostly seen from atomic adsorption on metal surfaces due to the formation of electric dipole moments on the surface. Ahn et al. observed that a new state N_1 of binding energy $E_b = 0.36$ eV develops in the stage I and its binding energy continues to shift to higher energy side up to $E_b = 0.56$ eV with increasing θ. They also observed that the surface state S_2 stemming from Si restatoms weakens quickly with θ while S_1 from Si adatoms and S_3 from adatom backbonds slowly weaken. With the formation of Na nanoclusters in the stage II, $\Delta\phi$ shows a much slower decrease with θ where new surface states N_2 of $E_b = 0.50$ eV and N_3 of $E_b = 1.10$ eV appear in photoemission spectra [13].

We present a series of HREELS spectra obtained from the Na adsorbed surface at various values of θ in Fig. 3. The spectra have been measured with a primary electron energy of 5.0 eV in a specular scattering geometry with incidence angle $\theta_i = 60°$. The bottom spectrum shows a Drude tail of metallic continuum due to the continuous electron-hole pair excitations from the S_1 state near Fermi level [15]. As soon as Na is adsorbed, the surface, however, becomes semiconducting as seen by the significantly reduced linewidth of the elastic peak at low θ (not shown). The surface eventually shows a band gap of 1.1 eV near 0.5 ML as reported earlier [14]. Interestingly we notice a quite broad bump centered around a loss energy $E_l = 300$ meV from the clean Si(1 1 1)-7×7 surface at 2° off from the specular angle (the second spectrum from the bottom in Fig. 3). This broad feature may be a loss peak produced by different scattering mechanism such as impact scattering [16]. As discussed later it, however, appears to survive with Na adsorption almost up to θ_2 where Na nanoclusters completely cover the whole surface. The most prominent loss peak associated with Na in Fig. 3 is the sharp loss peak with loss energy of 243 meV, which sensitively changes with θ. The spectrum shown in inset also show a new loss peak centered at 622 meV at $\theta = 0.282$ ML, unique only to the Na nanoclusters.

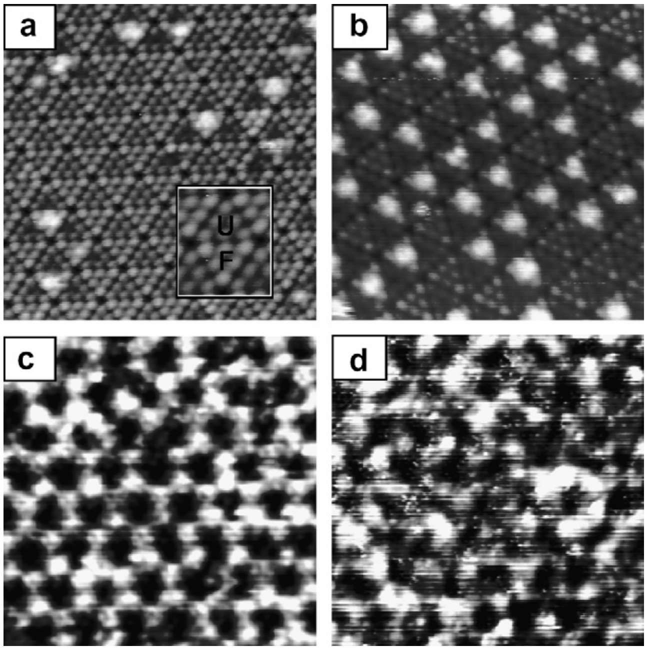

Fig. 1. STM images of the Na adsorbed Si(1 1 1)-7×7 surface at RT with coverage (a) 0.04 ML, (b) 0.12 ML, (c) 0.22 ML, and (d) 0.33 ML. Faulted and unfaulted halves of a Si(1 1 1)-7×7 unit cell are denoted by "F" and "U", respectively, in inset of (a). One finds that the sparse distribution of Na nanoclusters in (a) and (b) becomes a lattice-like array in (c).

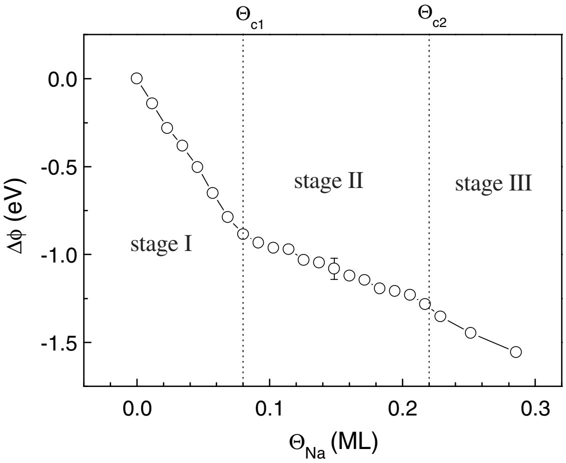

Fig. 2. Work function change ($\Delta\phi$) versus Na coverage (θ). There are three distinct stages I, II, and III corresponding to gas-like phase, lattice-like phase, and decayed phase of nanoclusters, respectively, as suggested by a previous STM study (Ref. [7]).