Adsorption/desorption kinetics of Na atoms on reconstructed Si (111)-7×7 surface

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A B S T R A C T

Self-assembled nanostructures on a periodic template are fundamentally and technologically important as they put forward the possibility to fabricate and pattern micro/nano-electronics for sensors, ultra high-density memories and nanocatalysts. Alkali-metal (AM) nanostructure grown on a semiconductor surface has received considerable attention because of their simple hydrogen like electronic structure. However, little efforts have been made to understand the fundamental aspects of the growth mechanism of self-assembled nanostructures of AM on semiconductor surfaces. In this paper, we report organized investigation of kinetically controlled room-temperature (RT) adsorption/desorption of sodium (Na) metal atoms on clean reconstructed Si (111)-7×7 surface, by X-ray photoelectron spectroscopy (XPS). The RT uptake curve shows a layer-by-layer growth (Frank-vander Merve growth) mode of Na on Si (111)-7×7 surfaces and a shift is observed in the binding energy position of Na (1s) spectra. The thermal stability of the Na/Si (111) system was inspected by annealing the system to higher substrate temperatures. Within a temperature range from RT to 350 °C, the temperature induced mobility to the excess Na atoms sitting on top of the bilayer, allowing to arrange themselves. Na atoms desorbed over a wide temperature range of 370 °C, before depleting the Si (111) surface at temperature 720 °C. The acquired valence-band (VB) spectra during Na growth revealed the development of new electronic states near the Fermi level and desorption leads the termination of these. For Na adsorption up to 2 monolayers, decrease in work function (−1.35 eV) was observed, whereas work function of the system monotonically increases with Na desorption from the Si surface as observed by other studies also. This kinetic and thermodynamic study of Na adsorbed Si (111)-7×7 system can be utilized in fabrication of sensors used in night vision devices.

1. Introduction

Nanoscale or atomic (molecular) scale structures constitute the key elements for various novel devices in nanotechnology and have provided unprecedented self-assembly to study exotic physics at low dimensions [1–12]. The evolution of the interface during the growth of metal nanostructures on the surface is an interesting field due to the metal induced surface reconstructions and their characteristic electronic and structural properties. The fabrication of nanostructures or the self-assembly of metal atoms on the surface, which depends upon the interactions between adsorbed atom and substrate properties, has widely been studied and applied to achieve large-scale growth of metal nanostructures. These metal nanostructures (nanowires or nanoislands) can be used fundamentally and technologically as a potential system for the fabrication of sensors and high-density memory devices [13–16].

From many decades, there has been a great interest in alkali-metal (AM) deposition on semiconductor and metallic surfaces, because of their electronic simplicity and hydrogen like atomic structure. The AM deposited surfaces are considered as a prototypical system for interface and, hence, several studies have been carried out to understand the key mechanism of AM growth on semiconductor surfaces [11,17–20] and these fundamental studies encourage possible technological applications, such as enhancement of photomultiplier tube in night vision devices and development of low work function material surfaces. A number of studies have been performed for the development of the AM nanostructure on various surfaces. Cesium (Cs) adsorption at room temperature leads to the formation of wire-like structures on the GaAs (110) surface [22,23] and also on InAs (110) and InSb (110) surfaces [24,25]. While Li forms nanoclusters at the initial coverage and all other AM (Na, K, and Cs) form two-dimensional (2D) gases at room temperature and coverage <0.08 monolayer (ML), on the Si (111)-7×7 surface [20]. Recently, Wu et al. have carried out the coverage dependent studies of Na atom on Si (111)-7×7, where they have observed the formation of 2D Na gas (for coverage up to 0.08 ML) followed by the growth of nanoclusters (for coverage in between 0.08 ML and 0.22 ML) on the Si (111)-7×7 surface [21]. However, they studied the initial stages of Na nanocluster formation whereas the kinetics of Na atoms for coverage >1 ML has not been fully explored.

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In the present study, we carefully carried out Na adsorption/desorption studies on the reconstructed Si (111)-7×7 surface, which can be treated as a possible template for the growth of ordered nanostructures due to hierarchy of preferred adsorption sites for the adatoms [9]. We performed kinetically controlled growth of Na atoms in the sub-monolayer regime, and study growth kinetics and work function change by in-situ X-ray photoelectron spectroscopy (XPS).

2. Experimental

The adsorption/desorption experiments were executed in a Perkin Elmer ultra high vacuum XPS chamber (Model 1257), at a base pressure of 5×10^{-10} torr. X-ray photoelectron spectroscopy (XPS) technique is used for identification of elemental composition and oxidation states. The chamber is equipped with a dual anode Mg-Kα (energy 1253.6 eV) and Al-Kα (energy 1486.6 eV) X-ray source and a high-resolution hemispherical energy analyzer for energy resolved electron detection. All binding energies (BE) were calibrated by the BE (284.6 eV) of Cls, which gave BE values within an accuracy of 0.1 eV. The sample is mounted on a high precision sample manipulator that enables its positioning for growth and analysis. A 20×10 mm² piece is cut from a p-type boron doped Si (111) wafer having a resistivity of 10–15 Ω cm.

The sample was cleaned by the modified Shiraki process [26] before inserting in the vacuum chamber. Sample was mounted on a 4-axis manipulator which clamped on a home made Ta sample holder. The sample was degassed to 600 °C for 12 h followed by repeated flashing up to 1100 °C for 5 s by electron beam heating and later cooling to RT at a very slow rate of 2 °C/s [10]. The sample temperature was monitored with the help of an optical pyrometer. The atomic cleanliness of a sample was ascertained by the absence of carbon and other contamination on the surface by XPS survey scan. Na deposition was made by home made tantalum–Knudsen cell assembly which includes a sodium chromate dispenser (Seas Getters). The flux rate of Na adsorption was controlled by regulating the current to the cell and measured in terms of the adsorbed monolayer. For optimal resolution survey scans and core level spectra are obtained at 100 eV and 40 eV pass energy respectively.

3. Results and discussion

Sodium is adsorbed on clean Si (111)-7×7 surfaces at room temperature (RT) and the formation of Na/Si interfaces was monitored by XPS. The uptake curve for the adsorption of Na on the Si (111) surface at RT is shown in Fig. 1, which plots the ratio of Na (1s) to Si (2p) peak intensity, with deposition time on the bottom X axis. The curve shows a linear increase in the ratio of Na (1s) to Si (2p) peak intensity up to a deposition time of 16 min. On further deposition a break in the slope is observed in the Na/Si intensity ratio i.e. the intensity ratio of Na/Si increases with Na adsorption with a slower rate. The break in the uptake curve suggests the formation of first Na ML on the Si surface and the change in the slope may have occurred due to the attenuation of the Si (2p) signal by the presence of second layer Na adatoms.

To calculate the actual break position in the uptake curve the sum of square of error method has been adopted (Fig. 1) which shows a minima in the slope of the Na/Si ratio (R_{Na/Si}) after 16 min of deposition time (R_{Na/Si} = 1.0), confirms the formation of 1 ML of Na (it refers to the in-plane atomic density of Si (111), i.e., 7.8×10^{14} cm^{-2}) [21] and also indicates that the adsorption rate is 0.0625 ML/min [27]. For better indications of the Na coverage on the Si surface, the top X axis is used to represent coverage in terms of ML. On further adsorption of Na, we observed another break at 32 min in the uptake curve which shows the completion of 2nd ML. Further deposition of Na atom on top of the 2nd ML reflects a decrease in the slope of the uptake curve, which suggests a possible interaction between Na–Na atoms and formation of Na clusters on top of the surface. The slope of the uptake curve suggests that the growth of Na atom follows a layer-by-layer (Frank van der Merwe) growth mode. A schematic model for such growth is shown in Fig. 1 at different data point of uptake curve.

To understand the interaction between Na adatoms and Si substrate, the high-resolution Na (1s) and Si (2p) core level spectra had also been acquired. From Na (1s) spectra, it is observed that the peak position of Na (1s) shifted to lower binding energy with increase in the Na coverage which has been shown as an inset in Fig. 1. The inset shows a change in the peak position of Na (1s) core level with coverage. A decrease of 0.45 eV is observed in Na (1s) peak position at coverage 0.125 ML and further decrease of 0.55 eV with deposition of another 1/4 ML of Na atoms. A total of 1.0 eV shift observed towards lower binding energy for initial 0.375 ML Na coverage. On further deposition of Na on Si leads to 1.33 eV shift in the Na (1s) peak position than its original value for the total coverage of 1 ML. For coverage 1.25 ML, Na (1s) peak shifted 1.38 eV towards lower binding energy and then remained constant for additional deposition. The shift in the Na binding energy position suggests a possible interaction between Na adatoms and Si substrate (metal–semiconductor interface), and can be attributed either to band bending at the interface or chemical bond formation between the adsorbate and the substrate.

The stability of this layer-by-layer grown Na/Si system is checked by annealing the substrate to increasingly higher temperature as shown in Fig. 2, which plots XPS intensity ratio of Na (1s) to Si (2p) with annealing temperatures. It is evident from the figure that on increasing the substrate temperature from RT to 350 °C, the R_{Na/Si} increases steadily, which suggests that the temperature induced mobility of excess Na atoms to rearrange and cover the bilayer. On increasing the substrate temperature beyond 350 °C, Na atoms start desorbing from the surface and a sharp decrease in R_{Na/Si} observed which can be attributed to the desorption of the Na multilayer from the Si surface. In the temperature range of 350–650 °C a continuous decrease in R_{Na/Si} value is observed which reveals that the Na multilayers are not stable for temperatures >350 °C and desorbed from the Si surface, depending upon the annealing temperature. As the annealing temperature reaches ~500 °C, a second monolayer desorbs completely and only one monolayer remains on top of the Si surface. On further increasing the temperature, the Na monolayer starts desorbing from the surface but the desorption rate is slower than that of in the case of bilayer. At 650 °C temperature, the R_{Na/Si} reduces to...
WF supports the metallic character of the Na/Si (111) interface system. In addition to this, we observed that WF changes from $-1.14$ eV to $-0.8$ eV when the coverage increase from 2.125 ML to 2.25 ML. We attribute this change in WF towards the local rearrangement of Na atoms on top of the two monolayers. The curve that shows change in WF follow the same behavior as observed by Wu et al. [21], but they reported $-2.3$ eV total change in WF for coverage in 20 min, which is $-1.35$ eV for 2 ML Na coverage in present case. Wu et al. explain sharp decrease in WF at initial coverage as formation of nano-clusters, which contributes in total change [21]. Change in WF during desorption of Na from Si surface is shown in Fig. 3. From room temperature to 500 °C, work function increases monotonically and change in WF increases from $-0.75$ eV to $-0.35$ eV. Beyond 500 °C, a sudden increase in WF was observed, and attains the original WF value for Si. This shows that the metallic character of the system is lost and it again turns out to be non-metallic. These changes in WF, during deposition or desorption process, corresponds to the compositional and chemical nature of the interface.

4. Conclusion

In conclusion, kinetically controlled adsorption/desorption of Na on the Si (111)-7×7 surface under the sub-monolayer regime has been investigated by X-ray photoelectron spectroscopy. The analysis shows the formation of Na/Si interface, where Na adsorption at RT follows the Frank van-der Merve (layer-by-layer) growth mode. Desorption studies revealed that on annealing the substrate to temperature 350 °C, Na atoms rearrange themselves and further increase in the annealing temperature causes desorption of Na atom from the Si surface. Na completely desorbed from the Si surface at temperature 720 °C. The systematic studies of change in WF show a decrease in WF with Na adsorption. In the present study, we tried to understand the solution to the ongoing puzzle of the change in WF at the sub-monolayer regime. The outcomes of the current study contribute to the fundamental understanding of a self-assembly mechanism of metals on periodic templates such as Si (111)-7×7.

Acknowledgments

The work is supported by the Department of Science and Technology (India) via grant (SR/FTP/PS-02/2006). One of the authors (AKS Chauhan) is grateful to the Council for Scientific and Industrial Research, India for providing fellowship under the CSIR-JRF scheme.

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