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SHG enhancement by roughness-induced surface plasmon excitation in alkali-metal overlayers grown on Si(1 1 1)-7 × 7

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ABSTRACT

Thin Alkali metal (AM) films of K, Rb, and Cs were grown on Si(1 1 1)-7 × 7, and second-harmonic generation (SHG) was observed at several wavelengths in the near-IR region at room temperature (RT) in an ultra-high vacuum (UHV) chamber. A large SHG signal was obtained for films deposited at low temperatures. This observation qualitatively agrees with the fact that films deposited at low temperatures are rough. For coverages above the saturation monolayer, resonance enhancement was identified centered at 2.5, 2.4 and <2.2 eV for K, Rb and Cs adsorption, respectively; these observations are in rough agreement with the reported resonance energies of surface plasmons.

1. Introduction

Alkali metal (AM) adsorption on Si surfaces has been the subject of numerous investigations in the past three decades. A wealth of information has been obtained on the electronic states of the AM/Si(1 1 1)-7 × 7 interface by using photoelectron spectroscopy (PES), inverse photoemission spectroscopy (IPS) [1–3] and electron energy loss spectroscopy (EELS) [4–6]. Despite the seeming simplicity of AM adsorption, however, the dynamics of adsorbate atoms and the geometric and electronic structures of the AM-covered silicon surfaces at coverage above a fractional monolayer (ML) still remain poorly understood.

Second-harmonic generation (SHG) is well suited for the study of AM growth because of the large SH signals originating from the large polarizability of AM atoms [7–12]. Previously, adsorption of Na, K, and Cs on Si(0 0 1) [7], Na [8], K and Cs [9,10], and Na and Li [11] on Si(1 1 1)-7 × 7 has shown remarkable SHG enhancement. The typical features of SHG reported for K and Cs adsorption at an incident photon energy of 1.17 eV include the first peak or a shoulder (peak A) for a coverage of ∼0.4 ML, the second peak (peak B) for a coverage of ∼0.9 ML, and a dip followed by a large signal (resonance C) for coverages >1 ML, where the coverage calibration was obtained by work function measurements [12]. Multiple SHG peaks of different origins have also been identified by the phase measurement of SH fields [12]. Polarization-selected SHG has been analyzed as a function of coverages obtained at photon energies ranging between 1.1 eV and 1.5 eV, and peak A has been attributed to the resonance enhancement due to transitions between AM-derived surface states formed by the hybridization of AM with Si; however, the origin of the latter peaks remains unknown [12]. Resonance C observed for AM overlayers has often been discussed in terms of resonance enhancement due to the excitation of surface plasmons [9,10]. However, there have been no reports on the direct spectroscopic observation of SHG.

It is well recognized that light illuminating a flat metal surface cannot directly couple with the surface plasmons, because the wave number of surface plasmons is always higher than the magnitude of the wave vector of the incident light parallel to the surface [13,14]. Molecules adsorbed on specially prepared silver surfaces are known to produce a Raman spectrum that is occasionally millionfold more intense than expected. This phenomenon is known as the surface-enhanced Raman scattering (SERS), which is usually attributed to the nonlinear effects of rough surfaces [15]. The mechanism responsible for this enhancement is assumed to be the roughness-induced excitation of surface plasmons by the incident light. This excitation in turn has increased the magnitude of the nonlinear source term in the Maxwell equations, which is responsible for the reflected light at twice the frequency of the incident light [15,16].

In this paper, we report for the first time the observation of resonant SHG due to the excitation of surface plasmons in layers with a large thickness. To this end, we reinvestigated the effects of K, Rb and Cs adsorption on Si(1 1 1)-7 × 7 in terms of the wavelength and coverage dependence of SHG. For coverages above the saturation

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monolayer, the observed resonances were in good agreement with the reported resonance energies of surface plasmons.

2. Experimental

The details of the experimental setup are described elsewhere [12]. The sample used in the present study was a 0.33-mm-thick P-doped Si(1 1 1) wafer. It was mounted in the [2 $\bar{1}$ $\bar{1}$] direction, one of the three mirror planes, lying at an angle of 30° relative to the plane of incidence in an ultra high vacuum chamber equipped for low energy electron diffraction (LEED) and Auger electron spectroscopy. Sharp 7 × 7 LEED patterns were observed when the sample was subjected to direct resistive heating at approximately 1400 K. The AMs were evaporated from well-outgassed dispensers (SAES Getters). The sample temperature was measured by a K-type thermocouple attached to the sample holder. Our LEED studies reproduced the previous observations [2,3] in that the saturated, monolayer-covered surfaces showed a 7 × 7 pattern at saturation coverage. The reduced quality, however, indicates a reduction of the long-range order.

SHG measurements were carried out using both the as-received wafer, i.e., without removing the oxide layer, and the clean Si(1 1 1)-7 × 7 surface. SHG was obtained by using an optical parametric laser (MOPO-730, Spectra Physics; duration 5 ns, pulse energy 1 mJ, repetition rate 10 Hz) at several wavelengths ranging between 1100 nm (1.13 eV) and 820 nm (1.51 eV) with a nominal bandwidth of 0.3 cm^{-1}. The wavelength of the reflected SH light was selected by a monochromator and detected by a photomultiplier tube connected to gated electronics. The laser was directed at an incidence angle of 45°. In the experiment, we measured the intensity of the *P*in*P*out SHG, where the *P*in*P*out signal, for example, indicates the *p*-polarized SH field for a *p*-polarized pump field. When both the input and the output polarizations are parallel to the plane of incidence (*p*-polarization), three tensor elements—χ_{xzx}, χ_{zxx}, and χ_{zzz}, with the *x* axis along the [2 $\bar{1}$ $\bar{1}$] direction and *z* axis along the surface normal—contribute to SHG [17,18]. While only χ_{xxx} tensor element contributes to the *P*in*S*out SHG [17]. χ_{xxx} describes rotationally anisotropic SHG, the existence of which requires an ordered surface, whereas the other tensor elements describe isotropic SHG, which can also exist on a disordered surface.

3. Results and discussion

SHG signals measured as functions of the coverage recorded for Rb adsorption on Si(1 1 1)-7 × 7 for *P*in*P*out polarization at three different pump photon energies at room temperature (RT) are shown in Fig. 1(a), and those for *P*in*S*out polarization at a pump photon energy of 1.17 eV are shown in Fig. 1(b). The *P*in*P*out SHG at 1.17 eV in (a) shows peak A, the second peak (peak B), and the dip followed by a large signal (resonance C) [9,12]. However, the dip and resonance C are either missing or very small at other photon energies. We also indicate the saturation coverage by 1 ML (monolayer) following Ref. [12], where the saturation coverage determined by the minimum value of the work function roughly corresponds to the dip. It should be noted that the *P*in*S*out SHG shown in (b), which depends only on the anisotropic non-linear susceptibility tensor component χ_{xxx}, disappears rapidly before the appearance of peak A during deposition. Moreover, peaks A, B and the following dip appear only for Si(1 1 1)-7 × 7 in contrast with deposition onto the as-received wafer [12].

Fig. 2 shows the SH intensities observed during AM deposition for 20 min on the samples at different temperatures for a pump photon energy of 1.17 eV. The temperatures depicted in the figure are those of the sample holder. These temperatures were measured at the onset of the AM adsorption onto the samples

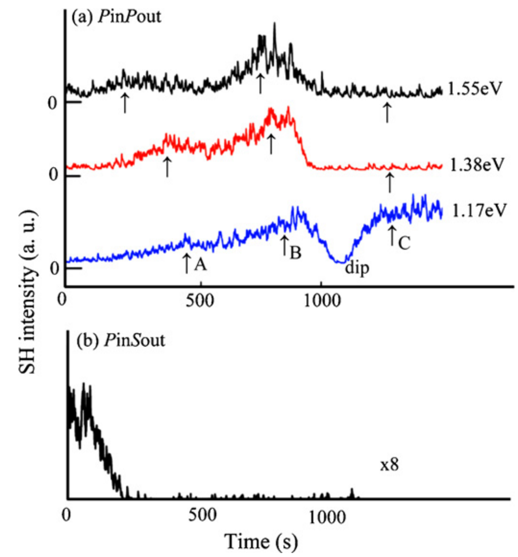

Fig. 1. SHG signals as functions of coverage recorded for Rb adsorption on Si(1 1 1)-7 × 7 at RT (a) for *P*in*P*out polarization at three different pump photon energies, and (b) for *P*in*S*out polarization. Arrows labeled A, B, C and dip indicate positions of typical features. Arrows with label C indicate the positions used for data analysis. Reprinted with permission from Ref. [12]. Copyright (2012) Elsevier.

as they were being cooled. First, we heated the sample by passing a fixed resistive current through it for a prolonged period and then let the sample cool down by switching off the current. The SH intensity of resonance C is sensitive to the substrate temperature, and is remarkably high for a substrate at low temperature. In a temperature-programmed desorption (TPD) experiment performed on Na/Si(1 1 1)-7 × 7, Boishin et al. [19] observed desorption from the multilayer Na structure even at RT. They attributed this desorption to the formation of 3D Na clusters having small binding energies. However, for a submonolayer coverage, desorption was observed only at temperatures above 500 K, with a single TPD peak centered around 700 K [19]. Moreover, the decrease in the binding energy of the adsorbed metal atom on metallic or

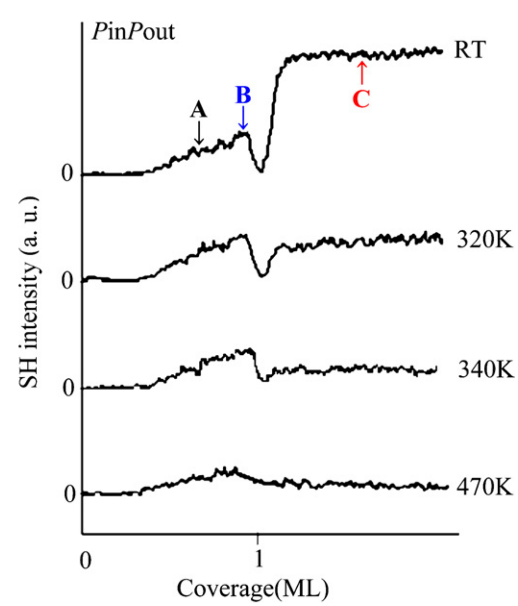

Fig. 2. SHG signals as functions of coverage recorded for Rb adsorption on Si(1 1 1)-7 × 7 for *P*in*P*out polarization at a pump photon energy of 1.17 eV and (a) RT, (b) 320 K, (c) 340 K, and (d) 370 K. Arrows labeled C indicate the positions used for data analysis.