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# Selenium adsorption on Cs-covered Si(100) $2 \times 1$ surfaces

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# Abstract

This report involves the study of Se adsorption on caesiated Si(100)  $2 \times 1$  surfaces in ultra high vacuum (UHV) using low energy electron diffraction, Auger electron spectroscopy, thermal desorption spectroscopy and work function measurements. Selenium atoms on Cs/Si(100)  $2 \times 1$  surface adsorb initially on uncaesiated portions of Si and subsequently on the Cs overlayer. The presence of Se increases the binding energy of Cs on Si(100). For Cs and Se coverages above 0.5 ml CsSe and Cs<sub>x</sub>Se<sub>y</sub>Si<sub>z</sub>, compound formation was observed. The coadsorption of Se and Cs induces a high degree of surface disorder, while desorption most probably causes surface etching. The presence of Cs on Si(100)  $2 \times 1$  surfaces prevents the diffusion of Se into the Si substrate and greatly suppresses the formation of SiSe<sub>2</sub> and SiSe<sub>3</sub>, detected when Se is adsorbed on clean Si(100)  $2 \times 1$  surfaces. © 2003 Elsevier Ltd. All rights reserved.

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### 1. Introduction

The properties of alkali metals on metallic and semiconducting surfaces and their interaction with electronegative elements such as oxygen have been the subject of numerous investigations [1–7]. In contrast to the case of oxygen, the coadsorption of alkali metals with the other elements in group VI on solid surfaces is very scarce [8–14]. The presence of alkali metals on metallic and semiconducting surfaces increases drastically the sticking coefficient and the maximum amount of oxygen on the surface and enhances its oxidation [2,4–7]. On the other hand, the presence of alkali metals does not change the sticking coefficient of S on Ni(100) [8,9,12].

Semiconductor compounds of Se have been receiving increased attention lately, due to their unique optical, structural and electrical properties [15,16]. Deposition studies of Se and compounds such as ZnSe, InSe and GaSe have been performed on surfaces of Si [15,17–19].

The coadsorption of Cs with S on Si(100)  $2 \times 1$  and Cs with Se on Si(111)  $7 \times 7$  surfaces have been performed very recently [10,14]. It is obvious that more scientific effort is necessary to understand the mutual effect of Se and alkali coadsorbates on Si surfaces.

In this investigation we study the adsorption of Se on caesiated Si(100)  $2 \times 1$  surfaces at room temperature. Data were acquired using the surface analysis techniques of low energy electron diffraction (LEED), Auger electron spectroscopy (AES), Thermal desorption spectroscopy (TDS) and work function (WF) measurements.

## 2. Experimental

The experiments were carried out in an ultra high vacuum (UHV) champer with base pressure  $\sim 10^{-10}$  mbar. The champer is equipped with a four grid LEED system, a hemicylindrical mirror analyzer (CMA) with a resolution of 0.3 eV for AES, a quadrupole mass spectrometer (UTI) for TDS an electron gun for WF measurements using the diode method and facilities for Ar ion bombardment.

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The Si(100)  $2 \times 1$  sample was cleaned by heating at 1300 K. The temperature of the sample was measured by a Cr–Al thermocouple calibrated by an infrared pyrometer in the range 900–1300 K. The surface was considered clean when the main impurity of carbon was below the detection limit of the Auger spectroscopy. The clean surface shows a very sharp  $2 \times 1$  reconstructed LEED pattern. Caesium was evaporated from a commercial dispenser source (SAES getters). Elemental Se was evaporated by thermal dissociation of WSe<sub>2</sub> single crystal flakes enclosed in envelopes of thin Ta plates which were heated by passing the required electrical current. The atomic Se produced by the source was estimated to be 30% of the total yield [14].

The respective dosages of Cs and Se were calibrated by analyzing the LEED and Auger spectroscopy data separately deposited on clean Si(100)  $2 \times 1$  surface at room temperature. The surface atomic density of a saturation layer (1 ml) of Cs and Se was considered equal to that of the outermost layer of Si(100)  $2 \times 1$  surface,  $6.8 \times 10^{14}$  atoms/cm<sup>2</sup>.

# 3. Results

Fig. 1 shows the Cs (563 eV) Auger peak-to-peak height (Ap-pH) as a function of Se doses after 0.5 and 1.0 ml of Cs deposition on Si(100)  $2 \times 1$  surfaces at room temperature. On the same figure we show the corresponding Si (91 eV) Ap-pH versus Se deposition. The Si (91 eV) Ap-pH decreases drastically at low Se doses and levels off at high Se coverages. On the other hand, the Cs (563 eV) Ap-pH is constant at low Se deposition and continuous to be constant at high Se doses for the Cs (0.5 ml)/Si(100) surface, while it decreases for Cs (1 ml)/Si(100) system. Analogous behavior has been observed for Se deposition on Cs-covered Si(111) surfaces [14]. A substantial difference between Se depo



Fig. 1. The Cs (563 eV) Ap-pH as a function of Se deposition on clean and Cs-covered Si(100) surfaces.

sition on Cs-covered Si(100) and Si(111) surface is that the Si (91 eV) Ap-pH decreases and almost disappears at high Se doses on Si(111) surface, whereas on Si(100) surface it levels off at a value, which is 25% of its initial value (clean surface) independent of Cs precoverage. The stability of Cs (563 eV) Ap-pH at low Se coverages indicates that the Se adsorption sites are different than that of Cs and there would be no masking of the Cs adatoms. At high Se doses (>10) Se begins to cover the Cs adatoms, for the Cs (1 ml)/Si(100) surface system and the Cs (563 eV) Ap-pH decreases.

Fig. 2 shows the change of the Cs (47 eV) Ap-pH versus Se deposition on Si(100)  $2 \times 1$  covered with 0.5 and 1.0 ml of Cs at room temperature. On the same figure we also show the Se (45 eV) Ap-pH versus Se deposition on clean Si(100) surface. Unfortunately, the Se (45 eV) Auger peak does not resolve from the Cs (47 eV) Auger peak. The Se (45 eV) Ap-pH during Se deposition on clean Si(100)  $2 \times 1$  surface increases with a continuous lower rate as the Se doses increase in agreement with previous results [17]. Selenium deposition on Cs-covered Si(100) surfaces causes a slight increase of the (45-47 eV) Ap-pH up to 0.5 ml of Se deposition. Higher Selenium deposition leads to a continuous decrease of the (45-47 eV) Auger peak. The initial increase of the (45-47 eV) Auger peak height as the Se adsorption increases indicates that the Se adsorbs on different adsorption sites and the intensity of the two peaks is added. This is in agreement with previous data of Se on Cs-covered Si(111) and Cs on S-covered Si(100) surfaces [10,14]. The decrease of the Cs (47 eV)-Se (45 eV) Auger peak height caused by Se deposition above 0.5 ml is attributed to a strong Cs-Se interaction, which results to a change of the chemical bond of Cs and Se and/or to a reorganization of the surface. As it was observed previously, the intensity of the Auger peaks which involves valence electrons as it is the Cs (47 eV) are substantially affected by the chemical bond [20].

The  $2 \times 1$  LEED pattern observed after Cs deposition disappears for Se coverages, higher than 0.5 ml. This result



Fig. 2. The Cs (47 eV) and Se (45 eV) Ap-pH as a function of Se doses on clean and Cs-covered Si(100) surfaces.

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indicates that the presence of Se leads to a disorder of the surface.

Fig. 3 shows the WF change of the Cs-covered Si(100)  $2 \times 1$  surfaces as a function of Se deposition. On clean Si(100), Se deposition causes an increase of the WF, up to a maximum value near 1 ml, with a subsequent small decrease in agreement with previous results [17]. Selenium on Cs covered Si(100) surface causes a drastic increase of the WF for all Cs coverages. This behavior is the same as that observed for Se deposition on Cs-covered Si (111) 7 × 7 surfaces [14], but it differs slightly to that of oxygen on Cs covered Si surfaces. At high Cs coverages (1 ml), on Si(100) or GaAs(100) the WF of the surface decreases with oxygen deposition at low oxygen exposures [6,21]. The difference of the WF change curve of Se on Cs-covered Si(100) surface in correlation to that of oxygen on Cs-covered Si(100) surface is attributed to the different interaction of oxygen and Se with the Cs-covered Si system. Oxygen atoms initially submerge under the Cs layer and interacts with Cs overlayer, whereas the Se on Cs covered Si(100) surface occupies different adsorption sites, and interacts initially with Si atoms to form SiSe. Another substantial difference on the WF curves between oxygen and Se deposition on Cscovered Si surfaces is that after Se adsorption the increase of the WF is so high that the WF turns back, close to its initial value of the clean Si surface. The same large increase of the WF has been measured after Se deposition on Cs-covered Si(111) surface [14]. Such large increase of the WF was not

Fig. 3. Work function changes of Se on clean and Cs covered Si(100)  $2 \times 1$  surfaces as a function of Se doses.

observed after oxygen exposure on Cs-covered Si surfaces [6,21]. This is attributed to different interaction of oxygen and selenium with the Cs/Si(100) surface system.

Fig. 4 shows a series of the Cs (133 amu) thermal desorption spectra after 1 ml of Cs deposition and subsequent Se adsorption. The presence of Se increases the binding energy of Cs in agreement with previous results [14]. The main desorption peak of Cs after 4 ml of Se deposition appears at around 1050 K.

Fig. 5 shows a series of SiSe<sub>2</sub> compound thermal desorption spectra after 2 ml of Se deposition on Si(100) surface covered with different amounts of Cs. The peak of SiSe<sub>2</sub> from Se/Si(100) system appears at  $\sim$  980 K. The presence of a very small amount of Cs (0.06 ml) shifts slightly the SiSe<sub>2</sub> TD peak to lower temperature. Higher Cs precoverages causes a drastic decrease of intensity of the SiSe<sub>2</sub> peak which disappears for Cs coverages higher than 0.5 ml. This is attributed to the strong Se-[Cs/Si(100)] interaction for Cs coverages higher than 0.5 ml, which leads to a reorganization of the surface in agreement with the results of Auger spectroscopy (Fig. 2) and LEED observations. The SiSe3 thermal desorption peak indicates almost the same behavior and we do not show it here. Analogous results have been observed previously for the system Se/Cs/ Si(111) [14]. On the other hand, the SiSe desorption peak is not affected substantially from Cs precoverage. The above results indicate that initially, the Se occupies different sites

Fig. 4. The Cs (133 amu) thermal desorption spectra after 1 ml Cs deposition from Cs/Si(100)  $2 \times 1$  and Se/Cs/Si(100) surface systems, at a constant heating rate.





Fig. 5. This figure shows the  $SiSe_2$  thermal desorption spectra desorbed from Se/Si(100) and Se/Cs/Si(100) surfaces, at a constant heating rate, from 300 to 1300 K.

from those of Cs and forms SiSe up to a Se coverage of 0.5 ml. Higher Se deposition leads to a strong Se–Cs–Si interaction which, prevents the diffusion of Se into the Si substrate and the formation of SiSe<sub>2</sub> or SiSe<sub>3</sub> compounds.

Fig. 6 shows the CsSe and Si<sub>2</sub>CsSe compounds thermal desorption peaks after Se deposition on Cs covered Si(100) surfaces. These compounds appear at about 1050 K for Se and Cs coverages higher than 0.5 ml. This temperature is the



Fig. 6. This figure depicts the TDS of  $Si_2CsSe$  and CsSe compounds, desorbed from Se/Cs/Si(100) surfaces, at a constant heating rate.

same as that of the main peak of Cs (Fig. 4). This means possibly that the CsSe are fragments of a  $Si_xCs_ySe_z$  compounds. This is supported by previous results of Se on Cs-covered Si(111) surfaces [14].

#### 4. Conclusion

In this investigation we study the structural and chemical interaction between Se, Cs and Si during Se deposition on Cs/Si(100)  $2 \times 1$  surface systems. The investigation took place in UHV utilizing the surface analysis techniques LEED, AES, TDS and WF measurements. Adsorption of Se on Cs/Si(100) surface system results in Se being initially adsorbed on sites different than that occupied by Cs up to 0.5 ml of Se deposition and forms SiSe compound. Higher Se deposition leads to a strong Cs-Se and Si-Cs-Se interaction, which leads to a disorder of the surface. The CsSe and Si-Se-Cs compounds are removed from the surface at about 1050 K. The presence of Se increases the binding energy of Cs on Si(100)  $2 \times 1$  surface, whereas the binding energy of Se remains approximately equal to that on the clean Si(100) surface. The presence of Cs prevents the diffusion of Se into the Si substrate and suppresses substantially the formation of SiSe<sub>2</sub> and SiSe<sub>3</sub>.

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