

Adsorption of Water on a Cesium Covered SrTiO₃ (100) Surface

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The paper describes the adsorption of water on cesium covered strontium titanate SrTiO₃ (100) surface. The interaction of water with the substrate is investigated by AES, TDS and work function measurements. The results show that water does not dissociate or react with cesium on surface. In contrast when simultaneous adsorption of water and cesium takes place on surface, interaction between the co-adsorbates occurs resulting in cesium oxide formation.

Keywords: Adsorption, cesium, water, strontium titanate, dissociation, Auger electron spectroscopy, thermal desorption spectroscopy, work function.

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82.80.Pv, 87.15.rs

1. INTRODUCTION

During last decades the adsorption of water at surfaces is a widely studied subject being presented by several excellent overviews [1,2,3]. The interest on water-surface interaction originates not only for the scientific reasons in order to understand better wetting and corrosion phenomena, but also for environmental concerns underlie the increasing importance of hydrogen as a fuel for green energy production.

Despite the scientific effort our knowledge of water adsorption remains incomplete. Strontium titanate SrTiO₃ is a perovskite with outstanding catalytic properties in photoelectrolysis of water [4]. Here we experimentally investigate the role of cesium as a promoter for water adsorption on the strontium titanate surface. The basis for the current work is the well known enhancement of the catalytic properties of metal oxides by the addition of alkali species.

2. EXPERIMENTAL PART

The experiments were performed in an ultra high vacuum system (UHV) at base pressure of 10⁻¹⁰ Torr. The system was equipped with Auger electron spectroscopy (AES), a quadrupole mass spectrometer (QMS) for the thermal desorption spectroscopy (TDS) measurements and a diode for work function measurements (WF). The sample was a strontium titanate, SrTiO₃(100) single crystal (STO) with dimensions 1cm×0.5cm×0.1cm. Cesium deposition was carried out by means of a commercial evaporation SAES Getters source at constant heating current 6 A. The H₂O adsorption on surface took place by supplying vapors of distilled water, into the experimental chamber through a leak valve. The water exposure was counted in Langmuirs (L), where 1L=1×10⁻⁶ Torr.s.

3. RESULTS AND DISCUSSION

3.1 Cs on STO(100)

For reference purpose we performed measurements of Cs adsorption on the clean STO(100) surface. The combination of AES and WF results indicate that Cs

forms a single layer on the surface showing the same behavior as that of Cs on metallic substrates [5], but different of that on semiconducting [6,7] and insulating surfaces [8]. At low coverages the Cs adatoms are strongly polarized, while at higher coverages depolarization effects between the adatoms lead to the metallization of the Cs overlayer. For cesium adsorption above one physical layer (1ML), the sticking coefficient drops to nearly zero. However, due to the high reactivity of Cs with oxygen, the prolonged existence of Cs on surface, accumulates significant amount of oxygen from the environment, increasing finally the maximum adsorbed quantity of Cs. The TDS measurements in Fig. 1 show the simultaneous grow of two high temperature thermal desorption (TD) peaks which appear from very low coverages. As the coverage increases both of the peaks grow further, while at the same time for coverage above 5 min deposition time, a low temperature TD peak starts to develop.

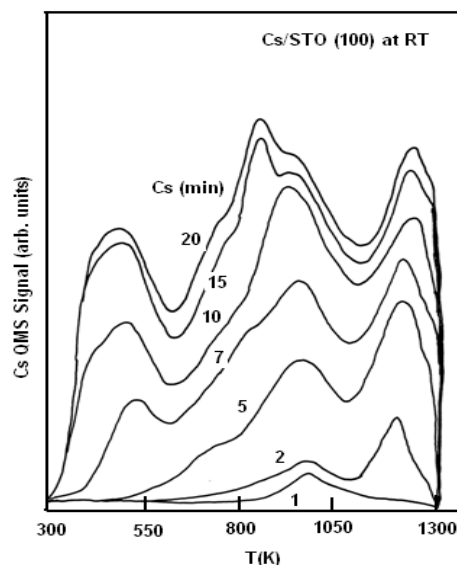


Fig. 1 – The TDS spectra for Cs adsorption on the STO(100) surface.

This peak is attributed to metallic Cs on surface which forms at coverage ~ 0.5 ML. TDS results reveal a different behavior of Cs on STO(100) than that on metallic substrates, where the high temperature peak saturates before the appearance of the metallic TD peak [9]. This means that Cs on STO(100) shows a mixed behavior between those on metallic and insulating surfaces.

3.2 H₂O on cesiated STO(100)

Next step was to adsorb H₂O on different cesiated STO(100) surfaces. WF measurements are shown in Fig. 2, where for predeposited Cs 10 min (~ 0.5 ML) and 40 min (more than 1 ML), the water adsorption on surface initially decreases the work function, while at higher exposures the WF increases. This behavior is similar to that of electronegative elements such as oxygen on Cs covered metallic surfaces [10]. The initial WF lowering does not happen for Cs 90 min. Instead, water adsorption on that surface causes only WF increase which resembles to the oxygen adsorption on cesium covered oxide surfaces [11].

TDS spectra of Cs after H₂O adsorption on the Cs(1ML)/STO(100) surface, showed that while the very high temperature TD peak does not change significantly the metallic TD peak shifts to higher temperatures as the exposure increases. This means that the presence of water on STO increases the binding energy of Cs on surface. On the other hand, the presence of Cs on the surface, increases the sticking coefficient of water. For Cs coverages above 0.5 ML, water desorption gives characteristic TD peaks at several temperatures. However, the main question is if the water dissociates with the presence of Cs on the surface. In that case Cs perhaps interacts on surface forming cesium oxide. To answer this question, we performed TDS spectra for Cs, H₂O, O and H₂, after H₂O exposure on cesiated Cs(20 min)/STO(100). As Fig. 3 shows, the Cs desorption does not coincide with those of H₂O, O and H₂.

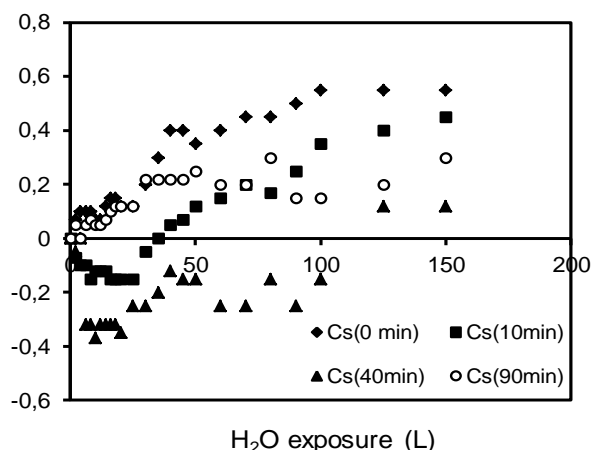


Fig. 2 – The WF change $\Delta\Phi$ of the Cs/STO(100) surface as a function of the H₂O exposure adsorption on clean STO surface, show part dissociation of water and oxidation of the substrate [13], while rapid dissociation of water has been also observed on cesium covered MgO(100) surface [14].

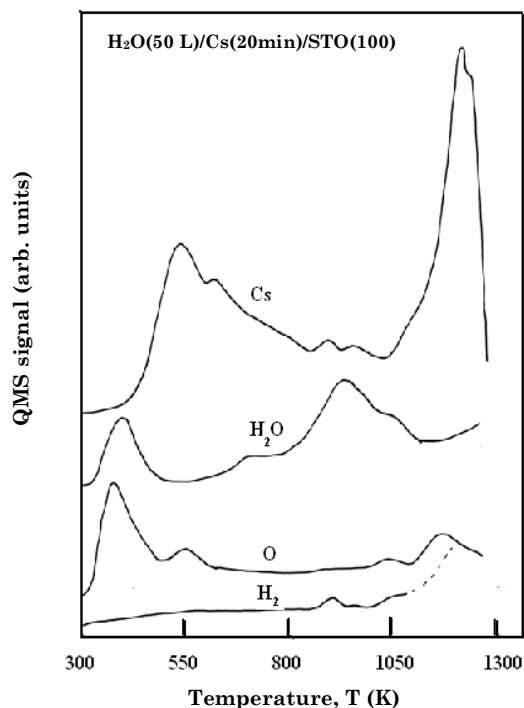


Fig. 3 – The QMS signal for Cs, H₂O, O and H₂, after H₂O exposure on cesiated Cs(20 min)/STO(100).

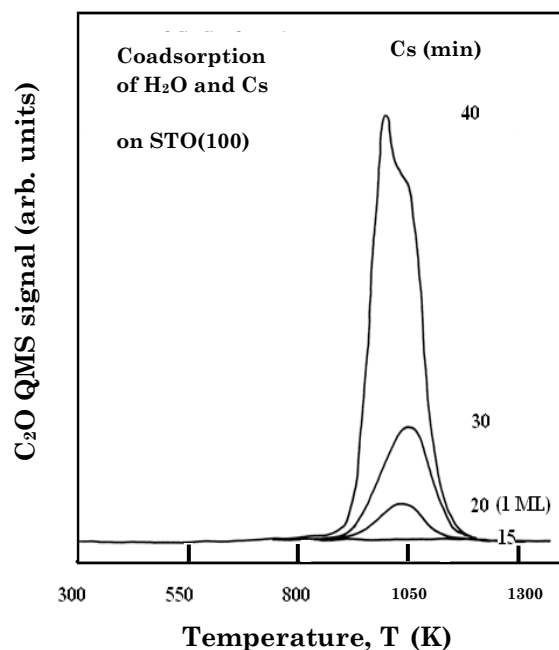


Fig. 4 – The QMS signal for C₂O, after H₂O and Cs simultaneous adsorption on the STO(100) surface.

Analogous results have been reported for water adsorption on potassium covered Si(100) surface [12]. This means that the H₂O does not interact strongly and does not form any Cs-H₂O compound. As a result we conclude that the water does not adsorb dissociatively on the cesiated STO surface. On the other hand, previous experiments of H₂O.

We also tried simultaneous deposition of Cs with H₂O on the STO(100) surface. Those experiments gave

the detection of Cs₂O in QMS signal as Fig.4 shows. It is important to note that the oxidation of cesium is observed if and only the corresponding Cs coverage is equivalent or larger than 1 ML. In that sense a prerequisite amount of Cs is needed in order to react with H₂O and form cesium oxide. From the above we conclude that codeposition of Cs with water can dissociate the molecule of H₂O on the STO(100) surface, resulting in the oxidation of Cs.

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4. CONCLUSIONS

The adsorption of Cs and H₂O was investigated on the STO(100) surface. The main conclusion is that when the Cs adsorbs first on the surface following water adsorption does not lead to the dissociation of the H₂O molecule. In contrast, when codeposition takes place the molecule of water dissociates resulting in the cesium oxidation.