



Low-temperature oxidation of alkali overlayers: Ionic species and reaction kinetics

David Krix, Hermann Nienhaus*

Faculty of Physics, University of Duisburg-Essen and Center for Nanointegration Duisburg-Essen (CENIDE), Lotharstr. 1, 47057 Duisburg, Germany

ARTICLE INFO

Article history:

Received 19 July 2012

Received in revised form 6 December 2012

Accepted 2 January 2013

Available online 1 February 2013

Keywords:

Sodium
Potassium
Rubidium
Cesium
Silicon
Oxygen
Oxidation

ABSTRACT

Clean and oxidized alkali metal films have been studied using X-ray photoelectron spectroscopy (XPS). Thin films, typically 10 nm thick, of lithium, sodium, potassium, rubidium and cesium have been deposited on silicon substrates and oxidized at 120 K. Plasmon losses were found to dress the primary photo emission structures of the metals' core lines which confirms the metallic, bulk like nature of the films. The emission from the O 1s core levels was used to determine the chemical composition and the reaction kinetics during the exposure to molecular oxygen at low pressures. Molecular oxide ions O_2^- and O_2^{2-} as well as atomic oxygen ions O^{2-} were detected in varying amounts depending on the alkali metal used. Diffusive transport of material in the film is shown to greatly determine the composition of the oxides. Especially, the growth of potassium superoxide is explained by the diffusion of potassium atoms to the surface and growth at the surface in a Deal–Grove like model.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

The interaction between oxygen molecules and alkali metal surfaces has been investigated in various context for the past decades. A strong technological interest exists as alkali metals have been identified as promoters in heterogeneous catalysis [1–3] and in the rapid low-temperature oxidation of semiconductor surfaces [4,5]. In addition, the alkali metal–oxygen compounds are candidates for low work function and negative electron affinity surfaces [6,7] and are relevant to nuclear fuels and fission products [8], especially for Cs and Rb. Nowadays, Li and LiO_2 are in the focus of intensive research and development activities for the purpose of designing batteries with extremely high specific energies of up to 3500 Wh/kg [9].

Likewise, the oxygen–alkali metal reactions are of fundamental importance. They are prototypical surface reactions with a strong non-adiabatic dissipation of chemical energy leading to chemiluminescence and the exoemission of electrons into vacuum [10–13]. Today, thin-film electronic devices can be used as internal hot charge carrier detectors [14–18]. They deliver a *chemi-current* due to chemically induced electronic excitations and have a much higher sensitivity than exoemission detection schemes. The recorded chemicurrents can be used to monitor the interaction

kinetics under reaction conditions [19]. To uncover the excitation mechanism it is essential to know whether dissociation of the oxygen molecule is necessary for the hot charge carrier generation and whether the degree of non-adiabatic dissipation changes with oxide growth. To answer those questions the oxygen uptake and the formed oxide species during the reaction must be known and characterized.

The present study is predominantly motivated by ongoing work on exoemission and chemicurrents during oxidation of alkali metals at low temperatures of 120 K. The oxidation of polycrystalline alkali metal layers deposited on Si substrates is investigated for Li, Na, K, Rb and Cs. The ionic species and the oxide growth modes are measured over a large exposure range. Lithium will be discussed as a special case due to the high penetration rate of the metal into the Si substrate. Despite their relatively simple electronic structure the alkali metals are able to form a great variety of oxides which led to the need of unambiguous identification of these species [20,21,22]. Different alkali oxide species can be created depending on the experimental conditions. Regular oxides M_2O need the dissociation of the molecule and contain O^{2-} ions. Molecular oxides are the peroxide M_2O_2 with O_2^{2-} ions and the superoxides MO_2 based on O_2^- ions. At surfaces the different oxygen ion species can be distinguished by X-ray photoelectron spectroscopy (XPS) as the binding energy of the O 1s core level depends unambiguously on the oxidation state of the metal. We make use of the data of earlier studies at thin alkali metal films from submonolayer to several nanometer thickness. The O 1s binding energy is found between 527

* Corresponding author.

E-mail address: hermann.nienhaus@uni-due.de (H. Nienhaus).

and 531 eV for the regular oxides, between 531 and 533 eV for the peroxides and between 534 and 535 eV for the superoxides [23,24]. The present article gives a comprehensive overview on the kinetics and on the exposure dependent formation of the various ionic species for all of five alkali metals during oxidation at 120 K. Since the different alkali metal films are prepared and treated under identical experimental conditions the kinetics of the reactions and the binding energies of the oxygen core levels can be directly compared. The latter obey a significant chemical trend related to the charge transfer between metal atoms and oxygen atoms/molecules.

2. Experiment

The experiments were performed under ultra high vacuum (UHV) conditions with a base pressure well below 10^{-7} Pa and using a SPECS Phoibos 100 hemispherical electron analyzer for ultraviolet (UPS) and X-ray photoelectron spectroscopy. The X-ray source was equipped with a Mg anode delivering non-monochromatized MgK α light with a photon energy of 1253.6 eV. The samples were prepared under UHV conditions in a separate preparation chamber equipped with a liquid nitrogen cooled cryostat. Before transferring into UHV, the thermally oxidized Si(001) substrates were cleaned and etched with 5% hydrofluoric acid (HF). Subsequently, they were again chemically oxidized and the thin oxide layer is removed by a final HF etch. Si wafers of both, *p*- and *n*-type doping were used. No charging of the samples occurs due to an ohmic back contact of the Si substrates.

The alkali metal overlayers were deposited from SAES dispensers onto the cooled hydrogen passivated Si(001) substrates at typically 120 K. The alkali film thickness was estimated from the attenuation of the Si 2*p* core level emission as approximately 10 nm. After metal deposition, the samples were quickly transferred to a coolable sample mount in front of the electron spectrometer. Oxygen exposures were made by backfilling the chamber using a precision leak valve. Exposures were determined by integrating the oxygen pressure over time. We used a Bayard–Alpert hot-filament pressure gauge located far away and line-of sight from the samples to prevent any excitation of the gas by the gauge. Throughout the article, oxygen exposures are measured in Langmuirs with $1 \text{ L} = 10^{-6} \text{ Torr s} = 2 \times 10^{14} \text{ molecules/cm}^2$. Binding energies of core levels are given relative to the Fermi level determined from UP spectra of a thick polycrystalline silver film deposited onto the same substrate. For fitting the core level features Voigt profile functions were used after a linear background subtraction.

3. Results

3.1. Sodium

Typical spectra of the Na 2*s* and Na 2*p* core levels are shown in Fig. 1 for the as-deposited and fully oxidized Na film. Additional features are observed for the clean surface due to single and multiple energy losses of the photoelectrons by the excitation of volume plasmons. In full agreement with earlier studies [25] the binding energies are found at 63.9 eV for Na 2*s* and 30.9 eV for Na 2*p* relative to the Fermi level. The plasmon energy E_p is determined as 6.0 eV. After oxidation the plasmon loss structures vanish and the Na core levels are shifted by 1.5 eV to larger binding energies. This shift indicates a strong bonding with significant charge transfer between sodium and oxygen which is typical for the atomic oxygen species. In fact, the O 1*s* core level exhibits a strong component of the oxide species (Na₂O) in the whole exposure range as shown in Fig. 2. The O 1*s* photoemission structure comprises two components which are assigned to the oxide at a binding energy of 529.2 eV and to the peroxide (Na₂O₂) at 533.0 eV. In the displayed spectra the background

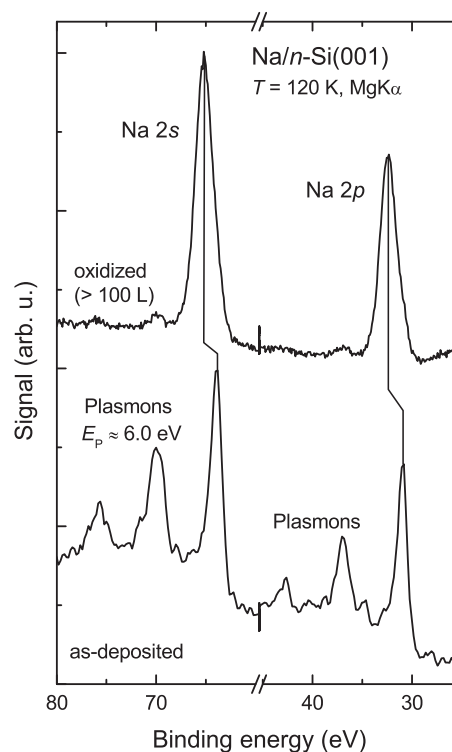


Fig. 1. Na multi-layered film deposited on *n*-Si(001) at 120 K. Sodium core levels for the as-deposited and the oxidized metal film.

is subtracted from the data and the solid lines is the sum of the two Voigt-type fitting curves (thin lines) for the different components. It is obvious that dissociation of the oxygen occurs on the pristine film and that the peroxide species increases with exposure and is eventually the dominating feature. In Fig. 3 the relative contribution of the two components to the total emission is shown by taking the area below the photoemission lines as the signal intensity. The

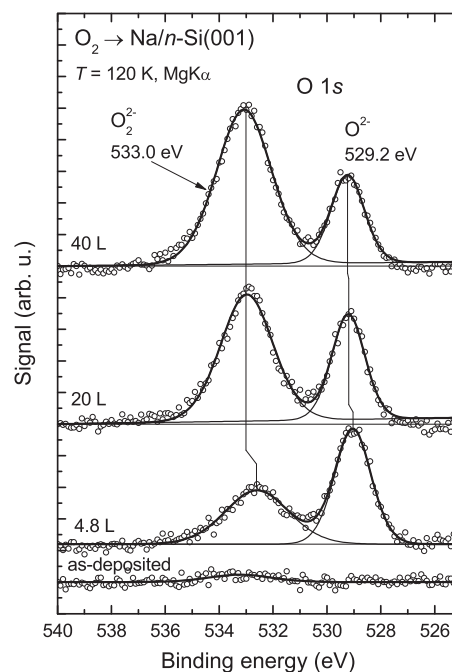


Fig. 2. Oxidation of a Na multi-layered film deposited on *n*-Si(001). O 1*s* photoemission structures after various oxygen exposures at 120 K.

Download English Version:

<https://daneshyari.com/en/article/5360415>

Download Persian Version:

<https://daneshyari.com/article/5360415>

[Daneshyari.com](https://daneshyari.com)