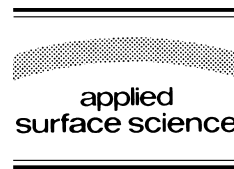




ELSEVIER

Applied Surface Science 127–129 (1998) 101–104



Photon stimulated desorption of cations from yttria-stabilized cubic $\text{ZrO}_2(100)$

D.P. Taylor^{1, 2}, W.C. Simpson², K. Knutsen², M.A. Henderson, T.M. Orlando^{*}

Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory, P.O. Box 999, M/S K8-88, Richland, WA 99352, USA

Abstract

The positive ion yield resulting from the interaction of a pulsed 266-nm laser with yttria-stabilized cubic zirconia crystals is investigated. Although the photon energy (4.66 eV) is well below the nominal band-gap energy for ZrO_2 (5.0–5.5 eV), photon stimulated ion desorption (PSD) of Y^+ , Zr^+ , YO^+ and ZrO^+ begins at $\sim 2.5 \text{ MW/cm}^2$. We interpret this as the onset of laser ablation. Cation mass spectra collected using higher laser fluences resemble those obtained via secondary-ion mass spectrometry (SIMS). The similarity between the laser ablation and SIMS data demonstrates the importance of surface electronic structure effects in photon induced degradation of this material. © 1998 Pacific Northwest National Laboratory. Published by Elsevier Science B.V.

Keywords: Laser ablation; Photon stimulated desorption; Cubic zirconia

1. Introduction

Zirconia (ZrO_2) is a wide band-gap ($> 5.0 \text{ eV}$) material which is used in a variety of applications. The cubic form of ZrO_2 is metastable at room temperature but can be stabilized by additives such as yttrium-, magnesium-, or calcium-oxides [1]. These metal oxides stabilize the crystallographic structure but also introduce oxygen vacancies and alter the electronic structure. Zirconia has novel electronic and chemical properties that make it an excellent

material for electrochemical applications such as fuel cells and oxygen sensors. In addition, it is often used as an optical coating since it is a full-valence ionic material thought to be highly resistant to radiation damage.

Damage from high-power pulsed Nd:YAG pumped dye lasers has generally been attributed to thermal and/or electronic processes. Though a number of studies on photon-induced damage of ceramic materials such as ZrO_2 have been reported [2,3], no general consensus concerning the mechanisms of ablation exists. The multi-hole model for the non-linear dependence of laser-induced desorption from wide band-gap materials with sub-gap photons involves two-hole localization at the surface [4–7]. Photons with energies near or above the band-gap energy can produce color centers in yttria-stabilized cubic zirconia which have been associated with elec-

^{*} Corresponding author. Fax: +1-509-376-6066; e-mail: tm_orlando@pnl.gov.

¹ Present address: The Aerospace, M5/753, 2350 E. El Segundo Blvd., El Segundo, CA 90245, USA.

² Associated Western University Postdoctoral Fellow.

trons occupying oxygen vacancies [8]. In the case of cubic ZrO_2 , high fluences of ultraviolet photons can produce high densities of electron–hole pairs. Two-hole states can form providing the lattice displacement energies exceed hole–hole Coulomb repulsion energies [4–7]. This can be enhanced by the high density of electron–hole pairs during laser irradiation since they further screen the Coulomb repulsion [4]. The states resulting from two-hole localization and lattice displacements can then induce desorption [4–7].

In this paper, we demonstrate that irradiation with sub-band-gap (266 nm) photons generates a measurable cation yield from yttria-stabilized cubic ZrO_2 . The onset of laser ablation appears at approximately 2.5 MW/cm^2 , as evidenced by the rapid increase in Y^+ , Zr^+ , YO^+ and ZrO^+ signal intensity. In this laser fluence regime, the PSD ion yield of these ions is superlinear in fluence and the cation mass distribution resembles secondary-ion mass spectrometry (SIMS) results obtained from identical crystals. The similarity between the laser ablation and SIMS data demonstrates the importance of surface electronic structure effects in photon induced degradation (ablation) of this material.

2. Experimental procedure

The PSD studies were carried out in an ultra-high vacuum (UHV) system equipped with a quadrupole mass spectrometer (QMS), an Auger electron spectrometer and a rotatable sample manipulator. A detailed description of this apparatus is published elsewhere [9]. The typical pressure was 2×10^{-10} Torr. Cubic $\text{ZrO}_2(100)$ crystals, doped with 9.5 mol% Y_2O_3 , were cleaned in vacuum by sputtering with 2-keV Ar^+ ions and then annealed to $\sim 850 \text{ K}$ by resistively heating the Ta foil that held the sample. The sputter/anneal cycles were repeated several times and surface cleanliness was checked with Auger electron spectroscopy.

The SIMS measurements were carried out in a separate UHV chamber. Identical samples were used, and surface cleaning was carried out in a similar fashion. SIMS spectra were obtained by bombarding the $\text{ZrO}_2(100)$ surface with 3-keV Ar^+ ions at an incident angle which was approximately 45° from

the surface normal. The desorbing positive ions were collected with a Bessel-box energy analyzer and detected with a QMS system.

The 266-nm fourth-harmonic light from a pulsed Nd:YAG laser was used in these experiments. The laser operated at 20 Hz with a pulse duration of about 7 ns. The time-averaged laser power was measured using a joule meter. In several of the experiments, loose focusing was utilized to provide a slightly higher laser fluence to the sample. Luminescence from the sample was exploited to provide an estimate of the diameter of the laser beam at the surface. The laser irradiance, which was determined from the power and beam diameter measurements, has an overall uncertainty of $\sim 50\%$, primarily due to the difficulty involved in determining an accurate beam size. The laser beam was introduced to the sample at an angle of 45° with respect to the surface normal. The desorbing ions were detected normal to the surface using the QMS, with its ionizer off and with a bias applied to the outermost element of its einzel lens assembly to increase the effective angle of acceptance. The PSD ion mass spectra are multiple-shot exposures carried out on initially virgin sites on the crystal.

3. Results and discussion

Fig. 1 shows a typical Auger spectrum from a clean zirconia surface. From this and similar spectra, we can place an upper limit on the relative concentration of impurities such as carbon, potassium and

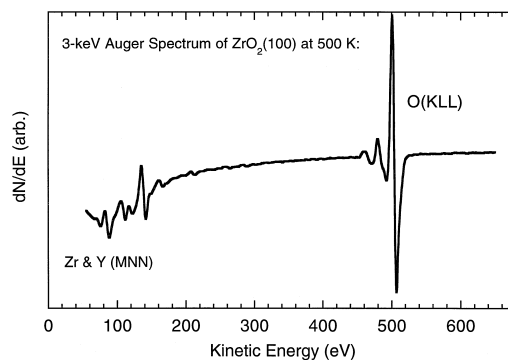


Fig. 1. A 3-keV Auger spectrum of yttria stabilized cubic zirconia. To prevent charging, the Auger spectra were collected at 500 K.

calcium at approximately 2%. Only Y, Zr and O features remain after repeated sputtering/annealing cycles. The intensities of the carbon KLL and calcium LMM Auger features, which are observed in the spectra of crystals prior to cleaning, fall below our detection sensitivity following cleaning. Note that it was necessary to keep the substrate temperature above 500 K during the collection of the Auger spectra to prevent charging.

Fig. 2 shows the PSD cation mass spectra collected at three different laser fluences. At 0.8 MW/cm², only masses 23 (Na⁺), 39 and 41 (K⁺) are observed. At 2.5 MW/cm², new peaks at mass 27 (Al⁺) and 40 (Ca⁺) are observed, and many low-intensity high-mass peaks appear where we expect to see Y⁺, Zr⁺, YO⁺ and ZrO⁺. Note that like K and Na, neither Al nor Ca are apparent in Auger electron spectra of the clean surface. Since they were not depleted by repeated cleaning cycles, we conclude that the K⁺ and Na⁺ signal results from trace contaminants in the bulk crystal. Similar low laser fluence desorption of alkali cations has been observed in PSD studies of other systems. By 2.9

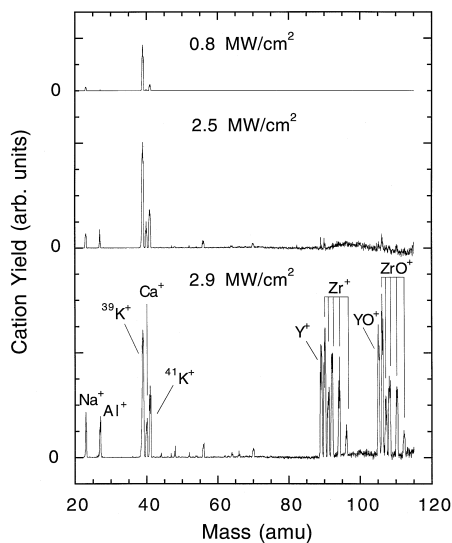


Fig. 2. Photon-stimulated desorption cation mass spectra obtained using 266-nm photons. The three frames represent three different laser fluences. Only desorption of K⁺ and other impurity ions is observed in the low fluence regime (0.8 MW/cm²). A small yield of yttrium and zirconium ions and their oxides are observable near 2.0 MW/cm². The yield of these species becomes appreciable above 2.5 MW/cm².

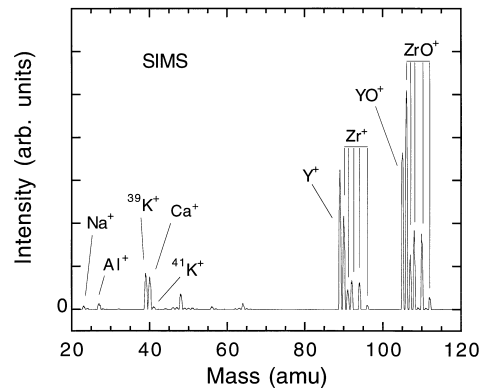


Fig. 3. Cation mass spectra obtained using secondary ion mass spectrometry. The incident Ar⁺ ion energy was 3 keV and the incidence angle was 45° from the surface normal.

MW/cm², a series of well-resolved peaks can be observed between mass 85 and 120, representing the many isotopes of yttrium and zirconium, along with their monoxides. Their intensities increase superlinearly with laser fluence. We interpret the appearance of the Y⁺, Zr⁺, YO⁺ and ZrO⁺ PSD signal as the onset of laser-induced ablation.

Fig. 3 shows the cation mass distribution from a SIMS measurement of an identically prepared crystal. As in the case of the ablation measurement in Fig. 2, Na⁺, Al⁺, Ca⁺ and K⁺ are observed along with the expected Y⁺, Zr⁺, YO⁺ and ZrO⁺ ion signal. In SIMS, the collision of the incident ion stimulates ion desorption through energy transfer, fragmentation and electronic excitations [10]. In energetic ion-surface collisions, the primary energy deposition is along the perpendicular velocity component and involves momentum transfer and electronic excitation of the substrate [10]. Therefore, cation desorption in SIMS results from complicated collisional processes involving both the formation of electron-hole pairs, charge deficiency regions (due to electron emission) and nuclear motion. SIMS does not involve a purely thermal desorption process.

The strong correlation between the observed cations and their relative intensities in the PSD and SIMS mass spectra suggests that similar mechanisms are responsible for cation desorption. Most models for laser ablation are independent of laser wavelength and depend only on the total energy deposited into a solid to produce thermal desorption [11]. Since

cation production and ejection in SIMS is non-thermal, the similarity in the ablation and SIMS data suggests that electronic excitations play a role in the laser ablation of ZrO_2 , especially near threshold. The similarity in the data further suggests that the final states leading to desorption during laser ablation and SIMS are ostensibly the same.

We suggest that the primary mechanism leading to (near threshold) laser ablation of yttria-stabilized cubic zirconia involves multi-hole localization, similar to that proposed by Itoh and Nakayama [4] and Hattori et al. [6] to explain PSD from GaP(110) surfaces. In materials with weak electron–lattice coupling, such as semiconductors and some metal oxides, self-trapping of holes and excitons does not occur. Rather, localization of energy can involve the production of multiple electron–hole pairs (via a multiple photon excitation) followed by two-hole localization at surface defects. Two-hole localization can occur when the hole–hole Coulomb repulsion energy (U) is less than the energy gained by lattice relaxation. These arguments are similar to the Anderson negative- U localization model for defects in the bulk [12]. Desorption occurs when at least two-holes are localized in the same bond.

This work will be extended by examining the neutral yields and quantum-state distributions using three excitation wavelengths: 355, 266 and 193 nm. Such studies will allow us to directly compare PSD behavior using sub-gap, and above gap excitations [13].

4. Conclusions

We have investigated the PSD of positive ions generated by the interaction of pulsed 266-nm laser light with yttria-stabilized cubic $\text{ZrO}_2(100)$ crystal surfaces. At low laser fluences (below $\sim 2 \text{ MW/cm}^2$) only trace impurities such as K^+ and Na^+ are observed, and the laser cleans the surface. The appearance of Y^+ , Zr^+ , YO^+ and ZrO^+ at

$\sim 2.5 \text{ MW/cm}^2$ is interpreted as the onset of laser ablation. In this laser fluence regime, the mass spectrum of cations produced by laser ablation resembles that generated by SIMS. We associate the desorption mechanism for both laser ablation and SIMS with the formation of two-hole states which decay at the surface.

Acknowledgements

This work was supported by Laboratory Directed Research and Development funds of Pacific Northwest National Laboratory and by the US Department of Energy, Environmental Management Science Program. Pacific Northwest National Laboratory is operated by Battelle Memorial Institute under Contract No. DE-AC06-76RLO 1830.

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