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Citation: Applied Physics Letters **86**, 091901 (2005); doi: 10.1063/1.1870103 View online: http://dx.doi.org/10.1063/1.1870103 View Table of Contents: http://scitation.aip.org/content/aip/journal/apl/86/9?ver=pdfcov Published by the AIP Publishing

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Interaction of atomic hydrogen with Zn-polar and O-polar ZnO surfaces

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(Received 15 October 2004; accepted 18 January 2005; published online 23 February 2005)

The interaction of Zn-polar and O-polar ZnO surfaces with atomic hydrogen produced by a remote rf plasma source is investigated *in situ* and in real time using spectroscopic ellipsometry. It is found that the reactivity of ZnO with atomic hydrogen depends on polarity. The interaction of O-polar surfaces with atomic hydrogen at 100 °C is suitable for producing clean surfaces, while Zn-polar surfaces strongly react with atomic hydrogen resulting in a disruption of the ZnO lattice with formation of Zn surface clusters. © 2005 American Institute of Physics. [DOI: 10.1063/1.1870103]

Hexagonal zinc oxide, ZnO, is a II-VI semiconductor of considerable technological interest for optics and optoelectronics due to its wide band gap of 3.4 eV, a strong excitonic feature even at room temperature and lasing properties at room temperature suitable for ultraviolet laser applications.¹ Furthermore, a number of other applications of ZnO-based systems are known in catalysis and for gas-sensor applications.² For all the above applications, it is of interest to study the interaction of ZnO with atomic hydrogen. Atomic hydrogen improves ZnO conductivity (up to eight orders of magnitude), passivates the green emission enhancing the band edge luminescence,³ and modifies the ZnO catalytic activity and adsorption of gases.⁴ Although a number of theoretical studies are devoted to the investigation of the interaction of hydrogen with ZnO,^{5,6} very few experimental investigations reported the real time monitoring of the interaction of O-polar and Zn-polar ZnO surfaces with atomic hydrogen and/or they do not characterize the different reactivity of the O- and Zn-polar ZnO. Mostly, previous studies^{7,8} investigated the change of conductivity and photoluminescence properties upon hydrogenation of ZnO. Hydrogen has been reported to diffuse very rapidly into ZnO even at temperatures of 100 °C. Hydrogen incorporation depths of $>15 \ \mu m$ at 200 °C by hydrogen plasmas have been reported,⁸ although it is not specified which polarity has been investigated. Specifically, the crystal structure of ZnO is wurtzite with two inequivalent sequences of atomic planes along the c axis, with the (0001) being the Zn-polar face and the (000-1) O-polar face. The Zn-polar and O-polar faces of ZnO are structurally and chemically different,⁹ and it has been reported that optical¹⁰ and electrical properties,¹¹ thermal stability,¹² impurity incorporation, doping efficiency,¹³ and the adsorption and reactivity of gases are influenced by polarity.

The present letter is aimed at providing further insight into the impact of ZnO polarity on the interaction of ZnO surfaces with atomic hydrogen produced by a remote rf H_2 . It is shown that the surface reaction of atomic hydrogen with ZnO is sensitive to ZnO polarity, being the Zn-polar surface is more reactive toward atomic hydrogen than the O-polar ZnO surface. The kinetics of the surface reaction of atomic hydrogen with ZnO is monitored in real time by spectroscopic ellipsometry (SE). One-side chemomechanically polished single-crystal ZnO(0001) and ZnO(000-1) wafers from Cermet, Inc. were used. The samples were exposed to an atomic hydrogen flux produced by a remote H₂ rf (13.56 MHz) plasma source. The H₂ plasma was operated at 60 W, 1 Torr and 800 sccm of H₂. Under these conditions, the atomic hydrogen density at the substrate position is $\sim 5 \times 10^{15}$ cm⁻³ corresponding to an atomic hydrogen flux impinging on the SiC surface of $\sim 4 \times 10^{20}$ atoms cm⁻² s⁻¹. Exposure of the ZnO surface to atomic hydrogen was performed at 100 °C, since a very high hydrogen incorporation depth has been reported even at a temperature as low as 100 °C.

Spectroscopic ellipsometric (SE) spectra of the pseudodielectric function, $\langle \varepsilon \rangle = \langle \varepsilon_1 \rangle + i \langle \varepsilon_2 \rangle$, were acquired from 1.5 to 5.5 eV (UVISEL-Jobin-Yvon) before and after exposure to atomic hydrogen of the ZnO surfaces. Measurements were carried out at angles of incidence of 60° and 65°. One-side polished substrates, both Zn face and O face, were used to reduce back reflection. ZnO is an anisotropic hexagonal crystal. However, for the present highly *c*-oriented single crystals, a mixture of the dielectric functions for the ordinary and extraordinary rays was measured for the optically anisotropic ZnO, and individual contributions were not separated. Even with a mixture, spectroscopic ellipsometry can be used for real-time monitoring during surface processing. Variation of the pseudodielectric function was monitored in real time at the photon energy of the excitonic transition during the atomic hydrogen treatment to monitor the ZnO surface modifications.

Ex situ x-ray photoelectron spectroscopy (XPS) analysis was performed using a Mg $K\alpha$ source to evaluate the surface chemical state upon the hydrogen treatment. Atomic force microscopy (AFM) measurements evaluated the surface morphology.

Figure 1 shows the spectra of the real, $\langle \varepsilon_1 \rangle$, and imaginary, $\langle \varepsilon_2 \rangle$, parts of the pseudodielectric function for the Znand O-polar ZnO wafers before and after exposure to atomic hydrogen. Before any treatment, a higher value of the excitonic transition is found for the O-polar ZnO. The effect of a surface overlayer is to decrease $\langle \varepsilon_1 \rangle$ and to increase $\langle \varepsilon_2 \rangle$ for all photon energies in our spectral range. The most abrupt, clean and ordered ZnO surfaces are those with maximized and minimized values of $\langle \varepsilon_1 \rangle$ and $\langle \varepsilon_2 \rangle$, respectively. The AFM analysis indicated approximately the same values for the two polar surfaces of the root mean square roughness and

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FIG. 1. (a) Spectra of the real, $\langle \varepsilon_1 \rangle$, and imaginary, $\langle \varepsilon_2 \rangle$, parts of the pseudodielectric function of Zn-polar and O-polar ZnO crystals. (b) Detail of the excitonic region in the $\langle \varepsilon_1 \rangle$ spectra for the Zn-polar and O-polar ZnO. A decrease and an increase of the exciton amplitude are found for the Zn-polar and O-polar surfaces with the increase of time exposure to atomic hydrogen: line with circles is for the starting surface; thick black line is after exposure for approximately 1 min; thin black line is after 10 min of exposure to atomic hydrogen.

peak-to-valley values (see Fig. 3). From this it is inferred that a different surface roughness is not responsible for the different ellipsometric spectra of the Zn- and O-polar ZnO wafers. The assumption of a surface contaminant overlayer in the fit analysis of the SE spectra yields a surface overlayer of approximately 5 and 80 Å for the O-polar and Zn-polar ZnO surfaces, respectively. This different reactivity to contaminant and, hence, the different SE spectra is consistent with first-principles studies of adsorption of CO on polar ZnO surfaces reporting that CO (and other C contaminants) energetically favorably binds to Zn ions present at the Znpolar surface with the "C-down" adsorption geometry, while binding of CO to surface oxygen ions at the O-polar surface is less favorable.⁴ Thus, the ellipsometric measurement of the different air-exposure reactivity of ZnO polar surfaces allows discerning the Zn-polar and O-polar ZnO surfaces.

Figure 2 shows the time variation of the real, $\langle \varepsilon_1 \rangle$, and imaginary, $\langle \varepsilon_2 \rangle$, parts of the pseudodielectric function of ZnO crystals of both polarities during exposure to a flux of atomic hydrogen at a temperature of 100 °C. It is found that the Zn- and O-polarity show opposite trends, and a larger variation is recorded for the Zn-polar surface that shows a fast modification even after approximately 30 min of treatment while the plasma treatment was terminated after 15 min for the O-polar surface because of the observed kinetic plateau. In particular, it is found that the O-polar ZnO is almost unreactive with atomic hydrogen; a very small $\langle \varepsilon_1 \rangle$ increase and $\langle \varepsilon_2 \rangle$ decrease, reaching a plateau value, after a few minutes, are observed. It is though that this observed variation is

FIG. 2. (a) Time variation of the real, $\langle \varepsilon_1 \rangle$, and imaginary, $\langle \varepsilon_2 \rangle$, parts of the pseudodielectric function recorded at the photon energy of 3.3 eV (corresponding to the ZnO exciton) during exposure of the Zn-polar and O-polar ZnO single crystals to atomic hydrogen. (b) Zoom of dashed area in (a).

simply related to cleaning/improvement of the O-polar ZnO surface. The improvement can also be seen in the increase of the excitonic transition in the $\langle \varepsilon_1 \rangle$ spectrum of Fig. 1 and in the minimization of the residual absorption below gap in the $\langle \varepsilon_2 \rangle$ spectrum ($\varepsilon_2=2nk$ where *n* is the refractive index and *k* is the extinction coefficient that is proportional to the absorption coefficient). In contrast, for the Zn polar, after a small $\langle \varepsilon_1 \rangle$ increase and $\langle \varepsilon_2 \rangle$ decrease due to surface cleaning, the trends reverse and a decrease of $\langle \varepsilon_1 \rangle$ and an increase of $\langle \varepsilon_2 \rangle$ without any saturation are found.

The observed different kinetic ellipsometric profiles are indicative of a different surface reactivity of the Zn-polar and O-polar ZnO(0001) surface toward atomic hydrogen. The O-polar surface shows a natural affinity for H atoms, and by adsorbing an H atom onto the O-polar surface it becomes more stable, as also predicted by total energy calculations.¹⁴ This unreactivity of the O-polar surface is consistent with He-atom scattering experiments that demonstrated that the O-polar surface exposed to hydrogen shows a hydrogen termination with a (1×1) diffraction pattern, which stabilizes the O-polar ZnO surface.¹⁵ Formation of hydrogen adlayers on the polar Zn-ZnO(0001) surface that becomes highly unstable for larger exposure to hydrogen and undergoes reconstructions and structural changes that destroys the lateral order of the ZnO crystal has been reported.¹⁶ Hydrogen adsorbed on the Zn-polar surface is so reactive that it is capable of reducing bulk ZnO units to metallic Zn, forming OH groups according to the exothermic reaction

$ZnO+H \rightarrow OH+Zn.$

The OH- and Zn–H species that are formed at the Zn-polar surface upon interaction with atomic hydrogen decompose and desorb at the relatively low temperatures of 380 and 540



FIG. 3. (Color online) 5 $\mu m \times 5 \mu m$ AFM images of the [(a), (b)] O- an [(c),(d)] Zn-polar ZnO surfaces before and after exposure to atomic hydrogen; (e) and (f) are the 1 $\mu m \times 1 \mu m$ AFM and surface potential images of the hydrogen treated Zn-polar surfaces. The 1 $\mu m \times 1 \mu m$ 3D view and corresponding line profiles of the Zn-polar surface after exposure to atomic hydrogen are also shown.

K, respectively,¹⁷ explaining the fast and nonsaturating kinetics observed in Fig. 2.

The damage and reduction to Zn of the Zn-polar surface have also been corroborated by AFM and XPS data.

Figure 3 shows AFM images of the Zn- and O-polar ZnO surfaces before and after exposure to atomic hydrogen. Before any treatment the surfaces of the ZnO wafer have many scratches and pits. The morphology of the O-polar ZnO surface is almost unchanged after the atomic hydrogen exposure consistently with the absence of reactivity highlighted by ellipsometry. In contrast, the morphology of the Zn-polar surface drastically changes upon interaction with atomic hydrogen and shows bumps/clusters and submicron pits approximately 100 nm in diameter and 5 nm deep. The detail in the 1 μ m \times 1 μ m image and the corresponding surface potential image with the line profiles put in evidence that the clusters, although they are higher than the ZnO surface, have a surface potential lower than the ZnO surface, while no variation of the surface potential is observed for the pits. Therefore, the pits are chemically equal to ZnO, while the clusters are chemically different from the ZnO surface, i.e., they are Zn cluster formed on the Zn-polar surface upon interaction with atomic hydrogen.

The chemical modification of the O-polar and Zn-polar surfaces has been corroborated using the high-resolution XPS spectra of the Zn $2p_{3/2}$ and O 1s core levels of the Znand O-polar surfaces. After exposure to atomic hydrogen, the O 1s spectrum of the O-polar surface shows oxygen bonded to zinc in the lattice identified at 531.3 ± 0.1 eV and an increase of the higher binding energy peak at 532.9 ± 0.1 eV indicative of OH on the sample surface.¹⁸ For the Zn-polar surface, the Zn $2p_3/2$ peak fit components at 1021.7-1022.1eV due to ZnO and an increase of the component at 1020 eV due to Zn are seen upon hydrogenation, consistently with the reactivity highlighted by ellipsometry.

In summary, the interaction of atomic hydrogen with Znpolar and O-polar ZnO surfaces has been investigated and monitored in real time by spectroscopic ellipsometry. It has been found that the reactivity of ZnO towards atomic hydrogen strongly depends on polarity. The interaction with the O-polar ZnO results in atomically flat and cleaned OH terminated surfaces. In contrast, Zn-polar ZnO strongly reacts with atomic hydrogen yielding lattice disruption and Zn clusters.

The authors dedicate this work to Dr. Giovanni Bruno at IMIP-CNR for his personal efforts in sustaining the authors during this research activity. The authors acknowledge Dr. Jeff Nause, President of Cermet, Inc., Atlanta GA, for providing the ZnO substrates. They also thank the Ministero dell'Istruzione, dell'Università e della Ricerca (MIUR) for financial support.

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