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XPS and UPS study on band alignment at Pt–Zn-terminated ZnO(0 0 0 1) interface

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ABSTRACT

The interface between Pt and Zn-terminated ZnO(0 0 0 1) was investigated by X-ray and ultra violet photoelectron spectroscopy in order to examine electronic band alignment. An angle-resolved X-ray photoelectron spectroscopy measurement of the clean ZnO(0 0 0 1) surface has revealed a downward band bending by 0.25 eV. The results of the valence band analysis show that the work function and the valence band maximum of clean ZnO(0 0 0 1) were 4.49 eV and 2.79 eV, respectively. Platinum was then deposited in several deposition steps onto a clean ZnO(0 0 0 1) surface up to 0.6 nm in thickness. After the deposition, the binding energy of Zn 2p doublet peak was shifted towards lower value by 0.77 eV, and the measured work function changed to 5.51 eV. As a result, the Schottky barrier height of Pt/ZnO(0 0 0 1) interface was 1.11 eV.

1. Introduction

Zinc oxide is a very important semi-conductive material that can be used for various applications such as ultra-violet light sensors, transparent conductive films for solar cells and displays, catalysts for methanol steam reforming and so forth [1,2]. The surface of single-crystal ZnO can be found in different orientations such as non-polar ZnO($1 0 \bar{1} 1$), polar O-terminated ZnO($0 0 0 \bar{1}$) and polar Zn-terminated ZnO(0 0 0 1) modifications [3]. The O-terminated ZnO($0 0 0 \bar{1}$) surface is composed of a hexagonal structure of oxygen anions O^{2-} in the topmost atomic layer and zinc cations Zn^{2+} in the second layer. The second layer is not exposed to the surface due to the size of the O^{2-} ions [4]. Similarly, the surface of ZnO(0 0 0 1) has a hexagonal arrangement of Zn^{2+} ions in the first layer, which is located on the relatively large O^{2-} structure of the second layer. In this case, the second layer of O^{2-} ions is partially influenced by the external environment due to the small size of Zn^{2+} ions.

The diversity of possible polar surface arrangements of ZnO reflects different chemical reactivity and electronic properties. Roberts and Gorte showed that thermal desorption properties of CO molecules from Pt films deposited on the different polar ZnO surfaces were different due to unequal interaction between Pt atoms and Zn^{2+} ions at the surface [5]. Nagata et al. reported that the Schottky barrier heights of Pt–Ru metal alloys on ZnO depend on the polarity of the ZnO surface, which was obtained by current–voltage (*I*–*V*) measurements [6].

The work function and electron affinity of Zn-terminated ZnO surface exhibit lower values than those of O-terminated ZnO surface [7]. The electronic band structure of the contact between deposited metal and ZnO substrate is very sensitive to the surface orientation of ZnO. In order to predict the electronic potential barrier height between metal electrode and ZnO semiconductor it is necessary to investigate the band structure of well defined ZnO surface with various amount of deposited metal. Generally, Schottky barrier height can be determined by the sum of a band bending value and an energy difference between conduction band minimum in bulk and the Fermi level [8]. Band bending of a depleted layer of a clean ZnO surface can be expected due to the presence of non-uniform surface charge distribution. Due to the difference in charge distribution in depth between Zn-terminated and O-terminated clean ZnO surfaces, band bending between two-differently terminated surfaces is different. Because of the electric field in the depleted layer, the band bending can be directly measured by angular resolved X-ray photoelectron spectroscopy (ARXPS).

In our previous work [9], the band alignment at the interface between Pt- and O-terminated ZnO($0 0 0 \bar{1}$) was investigated and the Schottky barrier height was determined to be 0.72 eV. This paper presents the investigation of the band alignment at the Pt/Zn–ZnO(0 0 0 1) interface by ARXPS and ultra-violet photoelectron spectroscopy (UPS) in an ultra-high vacuum (UHV) system.

2. Experiment

The measurement was performed in an UHV system at the background pressure of 10^{-7} Pa. A monochromatic Al K alpha radiation

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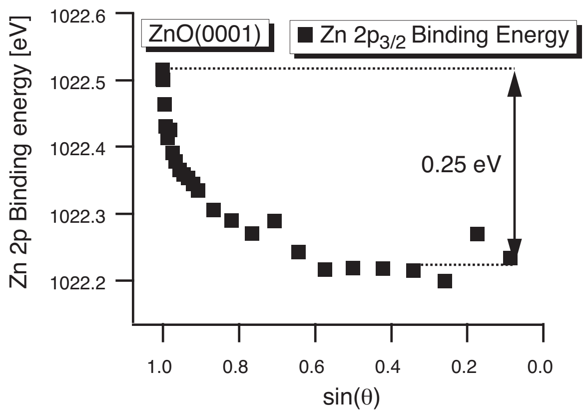

Fig. 1. ARXPS plot of Zn $2p_{3/2}$ photoelectron peak measured on clean ZnO(0 0 0 1) surface at room temperature.

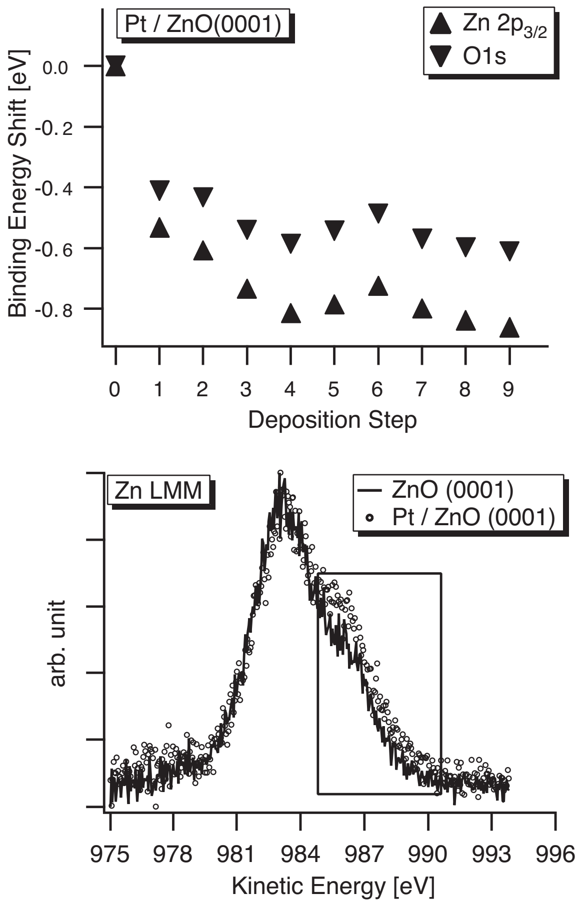

Fig. 2. Energy shift of Zn $2p_{3/2}$ and O 1s as functions of the deposition step (a). The Zn LMM spectra of the clean ZnO(0 0 0 1)and Pt/ZnO(0 0 0 1) surface, the marked area shows the difference between each spectrum (b).

source ($h\nu = 1486.6$ eV) was used for the XPS measurement. The detection of excited electrons was provided by PHI Model 10-360 Spherical Energy Analyzer. The angle between the photon source and the input lens axis of the analyzer was 90°. The UPS was measured with electrons exiting at the sample normal by the same electron energy analyzer. The source of the UV radiation was He I lamp ($h\nu = 21.22$ eV). The sample holder enables detection angles from 0° to 90° with respect to the sample surface normal. Work function values were obtained by measuring the low energy secondary electron cutoff in the UPS spectra under a bias voltage of −3 V applied to the sample.

A commercially available n-type single crystal ZnO(0 0 0 1) with the size ($10 \times 10 \times 0.5\,\text{mm}^3$) provided by TOKYO DENPA was used as a substrate. After a thermal flash at 800 °C, the sample was cleaned by several cycles of 700 eV Ar^+ ion sputtering for 10 min and subsequent annealing at 600 °C for 10 min in UHV in accordance with [10].

A platinum film was deposited on a clean ZnO(0 0 0 1) surface by an electron beam evaporator equipped with a flux monitor. A source was a platinum rod with diameter 1 mm stabilized by a tungsten wire winded around the rod. The absolute deposition rate was calibrated using the film thickness, which was calculated from Zn $2p_{3/2}$ peak intensity decay after each deposition step. The inelastic mean free path (IMFP) was calculated from the TPP2M formula [11]. The final thickness of Pt layer was calculated to be 0.6 nm. The possible surface contamination was checked after each deposition step by measuring C 1s XPS spectra and was considered to be at satisfactory low level. After subtracting Shirley background, the fitting of Zn $2p_{3/2}$, O 1s and Zn LMM spectra was performed by symmetric Voigt function. For Pt 4f metallic components, the asymmetric Doniach–Sunjich function was used. Because the Gauss distribution of secondary electrons, caused by the resolution of the energy analyzer, is assumed, the low kinetic energy cutoff position in UPS spectra was determined by finding a point, where a second derivation of a corresponding part of the spectrum equals zero.

3. Results and discussion

3.1. Core level peak fitting

The peak position of Zn $2p_{3/2}$ as a function of the detection angle θ of the clean ZnO(0 0 0 1) surface is shown in Fig. 1. The angle θ was measured from the surface normal. For the shallow electron escape angles, the binding energy of Zn $2p_{3/2}$ peak is shifted higher by 0.25 eV compared to the normal signal detection, which means that the band-bending occurs at the surface towards lower energy. This corresponds well with the band-bending of 0.22 eV previously observed for the clean ZnO(0 0 0 1) [3].

The Pt was deposited in a step-wise manner afterwards. The XPS spectra of Zn 2p, O 1s and Pt 4f levels and the AES spectra of Zn LMM Auger peak were obtained after each deposition step of platinum. The binding energy shifts and the changes in the area of the peaks were observed in order to study the chemical effects and possible changes in the band structure of the Pt–ZnO interface.

The difference in binding energy development between O 1s and Zn $2p_{3/2}$ peaks was found after simple analysis. Using only one component peak fit for Zn $2p_{3/2}$ and O 1s lines, values of energy shifts of these peaks with increasing number of deposition steps were not equal (Fig. 2a). In a case of energy shift due to the band bending caused by the Pt deposition, the parallel shifts for all elements of the substrate are expected. Therefore, the disagreement in values of each peak shift suggests the existence of additional components. Also the change in the shape of Zn LMM (Fig. 2b) peak supports the appearance of different chemical state of zinc. Referring to Zn LMM spectrum in [12], the arisen part of the Zn LMM peak in Fig. 2b was recognized to be metallic Zn. Because of the presence of metallic Zn in Zn LMM spectra, we did peak fitting assuming the partial reduction of ZnO and the formation of Pt–O bonding, as well as the band-bending.

Fig. 3 shows one example set of peak fitting of Zn $2p_{3/2}$ (a), O 1s (b), Pt $4f_{7/2}$ (c) and Zn LMM (d) peaks. The Zn $2p_{3/2}$ peak was separated into two components; one corresponds to zinc oxide (on higher binding energy) and the other one to metal zinc form (Fig. 3a). The approximate value of the metallic zinc component