Korean J. Electron Microscopy Special Issue 1, 41 ~ 46(2006)

Atomic Structure Analysis of A ZnO/Pd Interface by Atomic Resolution HVTEM

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(Received July 19, 2005; Accepted March 24, 2006)

ABSTRACT

Interfacial atomic structure (chemical structure) of a Pd/ZnO hetero junction was investigated by atomic resolution high voltage transmission electron microscopy (ARHVTEM). A misfit dislocation did not work as a stress accommodation mechanism in the ZnO (0001)/Pd (111) interface. But the periodic stress localization occurred in the ZnO $(10\bar{1}0)$/(200) interface. The periodicity of the local strain coincided with that of misfit dislocation. Atomic structure image of the ARHVTEM showed that an atomic arrangement across the interface was in the order of O-Zn-Pd. It was shown that mechanical weakness of the ZnO (0001)/Pd (111) interface against cyclic heating is attributable to the absence of the periodic stress localization of the misfit dislocation.

Key words : Atomic resolution, HVTEM, Misfit dislocation

INTRODUCTION

Mechanical weakness of a metal/ceramic hybrid material under cyclic heating during the work has been attributed to large difference of thermal expansion coefficient between metal and ceramic. Expanded atomic distance across the hetero interface due to heating accidentally goes over the threshold of atomic bonding to produce a crack. Previously employed method to solve this problem was to insert a cushion material which has intermediate thermal expansion coefficient value into the interface. But, it could not be the final solution of the problem. Mechanical strength of the cushion was not necessarily higher than any of the component materials in the other occasion. Melting point of the cushion was sometimes lower than that of the component metal. This method rather provided a new additional problem. More credible solution based on a physical principle has been desired. Despite not few people have discussed to give a clear solution in atomic dimension either experimentally or theoretically, the problem still remains unsolved (Mader, 1987; Lu & Cosandey, 1992; Muschik & Ruhle, 1992). Major cause of the situation is attributed to the lack of an experimental tool which enable the interface structure in real atomic dimension to observe.

In the present work a ZnO/Pd interface is observed by atomic resolution high voltage transmission electron microscope (ARHVTEM). The investigation is focused on the stress accommodation mechanisms of the interface in atomic dimension.

MATERIALS AND METHODS

A high purity Pd sheet 100 μm in thickness was alloyed by 2 at% Zn. The alloy sheet was heated at 1,273°K for 100 hours to make Zn solute in Pd. Following diffusion treatment the Pd-Zn alloy sheet was internally

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oxidized at 1,073°K for 14~37 hours in the air to obtain a ZnO precipitate in the Pd matrix.

The precipitated sheet was mechanically thinned down to 10 μm and then was thinned by Precision Ion Polishing System (PIPS). Incident angle of Ar ion of the PIPS was kept less than 4degree. Vacuum and acceleration voltage of the PIPS specimen chamber were respectively ~10^{-6} torr and 4 kV. Damaged surface layer produced during the thinning was brown off by five minutes irradiation of Ar at 2.5 kV acceleration.

The atomic resolution high voltage transmission electron microscope (ARHVTEM) was employed for the atomic structure investigation of the ZnO/Pd metal-ceramic hetero interface. The resolution of the microscope is 0.1 nm at the optimum focus condition (so called Scherzer condition) and the information limit of this machine extends over 0.09 nm (Ichinose et al., 1999), which are enough power to investigate the atomic structure of the ZnO/Pd hetero interface. Observation was performed at 1250 kV acceleration and 39 nm defocus, corresponded to the optimum focus condition. Not only atomic structure image but also ordinary lattice image was effectively employed depending on the required information level.

RESULTS

1. Chemical structure image of a crystalline ZnO

Super high resolution of the ARHVTEM enabled to observe chemical structure of the ZnO crystal as shown in Fig. 1. The picture image was obtained from 3 nm thick specimen at Scherzer focus condition so that atomic potential in the specimen was directly projected on the image in dark contrast (Horiuchi, 1988). The atomic structure image is highly qualified for the atomic structure investigation in comparison that an ordinary lattice image which is obtained from thicker specimen and shows only periodicity of atomic potential. A line profile of darkness along the Zn-O atomic pair (bottom left) of the picture (bottom right) consisted of two peaks. The higher peak corresponded to Zn and the lower one to O i.e. Zn appeared in darker thick contrast and O in brighter thin contrast. The intensity profile of a simulated image computed by multi-slice method, shown in upper half of Fig. 1, well coincided with that of experimental result.

2. Absence of misfit dislocation in the ZnO (0001)/Pd (111) interface

Although most developed surface of a ZnO crystal

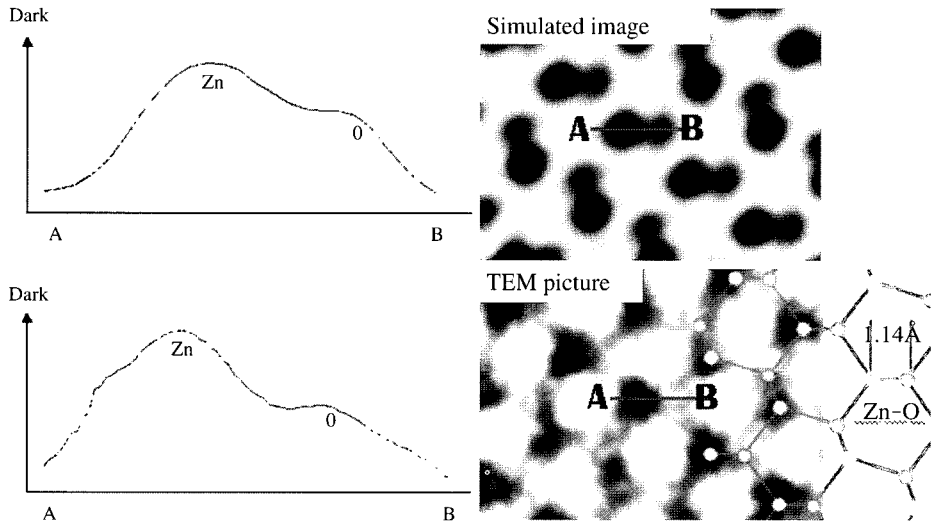

Fig. 1. Chemical structure image of ZnO crystal and elemental identification. Taking a darkness profile, the darker contrast corresponds to Zn and the thinner to O.

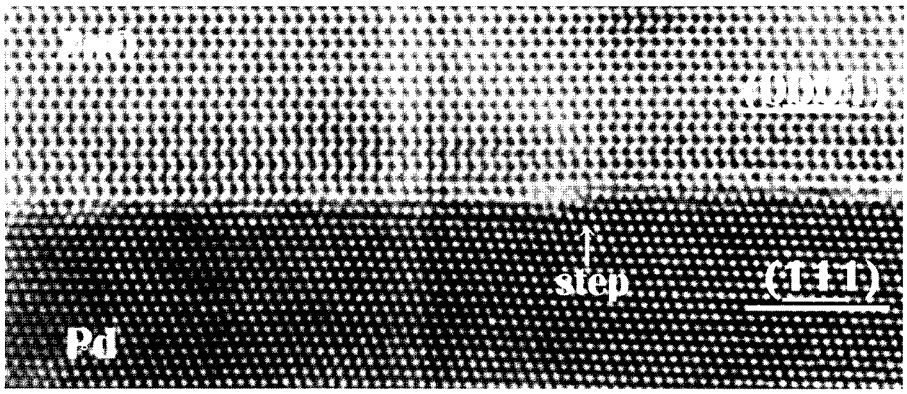

Fig. 2. Well defined ZnO/Pd interface being parallel to (0001) of Zn and to (111) of Pd. No periodic local strain contrast corresponding to a misfit dislocation is seen in the image. An atomic step is indicated by an arrow.

grown in the free space is $(20\bar{2}1)$ plane, the (0001) plan exceedingly developed in the Pd matrix. The development of (0001) plane of the precipitate ZnO is attributable to the energy reduction effect of the ZnO/Pd interface. Integrated inter atomic interaction energy over the interface area of the ZnO (0001)/Pd (111) junction must be lowest among the possible other ZnO/ Pd interfaces to present. Morphology of the interface was flat (or straight) in atomic dimension, showing well defined atomic arrangement (Fig. 2).

Lattice image of the ZnO (0001)/Pd (111) in Fig. 2 shows that the interface is well defined everywhere in spite of 14% lattice mismatch. The 14% lattice mismatch, according to O-lattice model (Bollman, 1980), must introduce a misfit dislocation at every eight (111) planes of Pd along the interface. And the introduced dislocation is expected to localize the stress around the core to release the stress in the other region. The interface structure is stabilized by this mechanism. Additional thermal stress, if supplied, is absorbed by sliding of the dislocations. In the present interface, however, no atomic site shift parallel to the interface producing localized strain field of the misfit dislocation, was observed in the lattice image of high resolution TEM (Fig. 2). That is, no strain localization around the misfit dislocation seems present. An absence of the local periodic strain localization means that no stress accommodation mechanism works in this interface. Under this situation inter atomic distance across the interface changes from place to place.

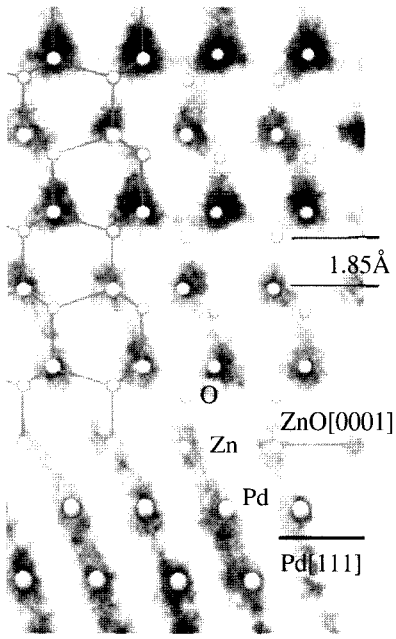

Fig. 3. An atomic structure image of the ZnO/Pd junction. Chemical structure is obtained following the procedure shown in Fig. 1. A largest spot in the bottom corresponds to Pd site, a medium spot to O and the smallest one to Zn. ZnO is terminated by Zn at the interface.

3. Chemical structure of the ZnO/Pd interface

Employed an atomic structure image which is observed under strict optical condition, namely less specimen

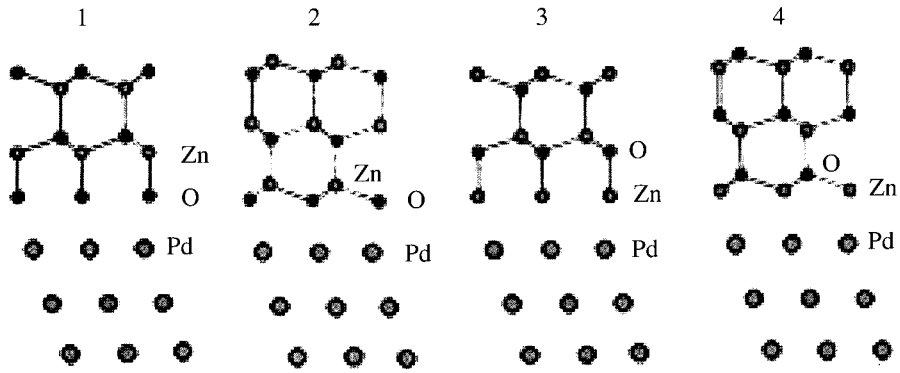

Fig. 4. Candidate geometrical structures of the ZnO/ Pd interface. The #3 showed good coincidence with the picture.

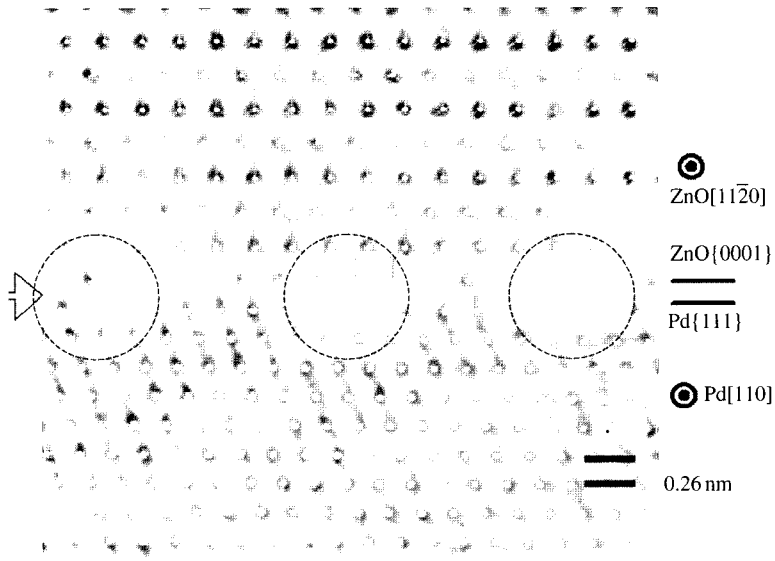

Fig. 5. Chemical structure image of the ZnO/Pd junction in wider region. Locally diffused region is periodically seen, corresponded to misfit dislocations.

thickness than 30 nm, a super high resolution TEM with 0.1 nm resolution, strict optical axis alignment, an obtained data (picture) will be capable of not only atomic structure analysis but also chemical structure investigation (Bollman, 1980). Pictures shown in Fig. 1 and Fig. 4 fulfill the required condition of the structure image. Chemical structure of the ZnO(0001)/Pd(111) interface was investigated by the image of Fig. 4 following the principle shown in Fig. 1. A larger spot was put at Zinc position and a smaller at Oxygen position in the ZnO region of the picture. Largest size dot was put at Pd position in the bottom region. Connecting each spots an atomic network was completed (Fig. 4). It was shown from the result that ZnO was terminated by Zn (not by O) at the interface even though there were four possible candidate model s in geometry as shown in Fig. 5. Among the four models, Zn connects to Pd in the model #3 and #4. In the #4, however, geometrical structure does not coincide with the present picture. The model #1 and #2 are totally not the case.

Fig. 6. Local stress accommodation of ZnO (1$\bar{1}$01)/Pd (200) interface by putting of local strain. Local atomic displacement near the dislocation core is apparent in (b).

4. Periodic interface structure

Atomic structure image (Fig. 5, projected potential image) in the wider region was inspected in order to see further precise structure which was hidden in the lattice image of Fig. 3, being lattice image. Atomic site was successfully pointed out in most area following the procedure shown in Fig. 1 but in some small region an image contrast was rather diffused to identify each atomic column. An extent of the unclear diffused region was at most several (111) planes of Pd in diameter (encircled by doted line in Fig. 5). No characteristic feature such as atomic site shift was detectable in the clear image region. Each atomic plane which was either parallel or intersecting to the interface appeared straight. The straight atomic row tells that there is no local elastic strain field. A periodicity of the diffused region coincided with that of misfit dislocation. The diffused image in Fig. 5 is attributed to slight irregular atomic displacement. In this region, ordinary local atomic bonding may not be expected in the region.

In the case that the interface was parallel to (1$\bar{1}$01) plane of ZnO and (200) plane of Pd, periodic strain localization occurred (Fig. 6(a)). An atomic arrangement of this structure is more apparent in the magnified image of enclosed region of Fig. 6(a), shown in Fig. 6 (b). Several (111) atomic planes of Pd in the vicinity of an extra half plane were apparently curved. Atomic rows in between the "dislocation" look straight showing that the extended strain over the interface was localized around the extra half plane or the dislocation core. A periodicity of the local strain was well coincided with that of misfit dislocation predicted by O-lattice model. The misfit dislocation seems to work as a stress accommodation mechanism in this interface.

DISCUSSION

To be noted in the present result is that the efficiency of misfit dislocation on the stress accommodation depended on the interface orientation even in the same materials. The periodic stress localization by the misfit dislocation did not occur in the ZnO (0001)/Pd (111) interface (Figs. 2, 5) but it did in the ZnO (1$\bar{1}$01)/Pd (200) interface (Fig. 6). Geometrical parameter seems to control the interface structure. However, the geometry can not be an essential cause. Physical contents which is adjoined (is represented) by the geometrical parameter can be an essential cause. In the present system hetero-

geneous bonding nature and rigidity of ZnO crystal influenced on the result. Although a Pd crystal may show the heterogeneity, a ZnO crystal is more clearly orientation dependant. The reason why the strain localization did not occur at the dislocation core in the ZnO (0001)/Pd (111) interface is that atomic bonding across the interface was not enough to provide strong component force which was parallel to the interface to pull atoms to the dislocation core. In the other words, rigidity of the component materials in the direction parallel to the interface surmounted the applied component force and kept the original structure. If the atomic bonding across the interface is stronger and rigidity of the component material in the direction parallel to the interface is lower the misfit dislocation may concentrate the nearby strain to the core region to accommodate the misfit stress as is shown in the ZnO ($1\bar{1}01$)/Pd (200) interface.

SAMMARY

Well defined ZnO/Pd interface was produced and atomic structure was investigated by ARHVTEM. The followings were shown. A misfit dislocation may not work as a stress accommodation mechanism in the ZnO (0001)/Pd (111) interface. However, it should work in the ZnO (1101)/Pd (200) interface. The atomic arrangement across the interface was in the order of O-Zn-Pd. It is suggested that the absence of stress (and strain) localization of the misfit dislocation may cause fragile interface.

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