

ATOMIC SCALE INVESTIGATION OF METAL/CERAMIC INTERFACE FRACTURE BY SUPER HIGH-RESOLUTION ELECTRON MICROSCOPY

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ABSTRACT

Interfacial atomic structure (chemical structure) of a Pd/ZnO hetero junction was investigated by atomic resolution high voltage transmission electron microscopy (ARHVTEM) in order to clarify the cause of thermal fracture of a metal/ceramic interface. A misfit dislocation, predicted by O-lattice model of Bollman, did not work as a stress accommodation mechanism in the ZnO(0001)/Pd(111) interface which was a polar interface. But in the non polar ZnO($10\bar{1}0$)/(200) interface periodic stress localization occurred. 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 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

thermal fracture, metal/ceramic interface, misfit dislocation, stress accommodation mechanism, bonding strength, high-resolution electron microscopy, chemical structure

INTRODUCTION

Although metal/ceramics hybrid materials are widely used, namely surface coating, electron device packages, and wirings to the semiconductor, a well known weak point problem still remains unsolved i.e. a metal/ceramic hybrid material is broken at the junction by cyclic heating during the work. A cause is known. The brittle junction has been attributed to large difference in 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. But, what ever cushion material is used it could not be the final solution of the problem. Melting point of the cushion was sometimes lower than that of the component metal. Mechanical strength of the cushion was not necessarily higher than any of the component materials in the other occasion. It rather provided a new additional problem. More credible solution based on a physical principle has been desired. Despite not few people have discussed so far to give a clear solution in atomic dimension either experimentally or theoretically, the problem still remains unsolved [1]. Major cause of the situation is attributed to the lack of an experimental tool to analyze the interface structure in real atomic dimension.

In the present work a ZnO/Pd interface is observed by our atomic resolution high voltage transmission electron microscope (ARHVTEM). This microscope enables us to observe even chemical structure of the hetero interface. The investigation is focused on the stress accommodation mechanisms of the interface in atomic dimension.

EXPERIMENTS

A high purity Pd sheet 100 μm in thickness was alloyed by 2at% Zn. The alloy sheet was heated at 1273K for 100 hours to make Zn solute in Pd. Following diffusion treatment the Pd-Zn alloy sheet was internally oxidized at 1073K 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 $\sim 10^{-6}$ torr and 4kV. Damaged surface layer produced during the thinning was brown off by five minutes irradiation of Ar at 2.5kV 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 0.1nm at the optimum focus condition (so called Scherzer condition) and the information limit of this machine extends over 0.09nm [2], which are enough power to investigate the atomic structure of the ZnO/Pd hetero interface. Observation was performed at 1250kv acceleration and 39nm 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

Chemical structure of ZnO crystal

Super high resolution of the ARHVTEM enabled to observe chemical structure of the ZnO crystal as shown in figure 1. The picture image was obtained from 3nm thick specimen at Scherzer focus condition so that atomic potential in the specimen was directly projected on the image in dark contrast (called as a projected potential image or atomic structure image)[3]. The atomic structure image is highly qualified for the atomic structure investigation in contrast to 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 figure1, well coincided with that of experimental result.

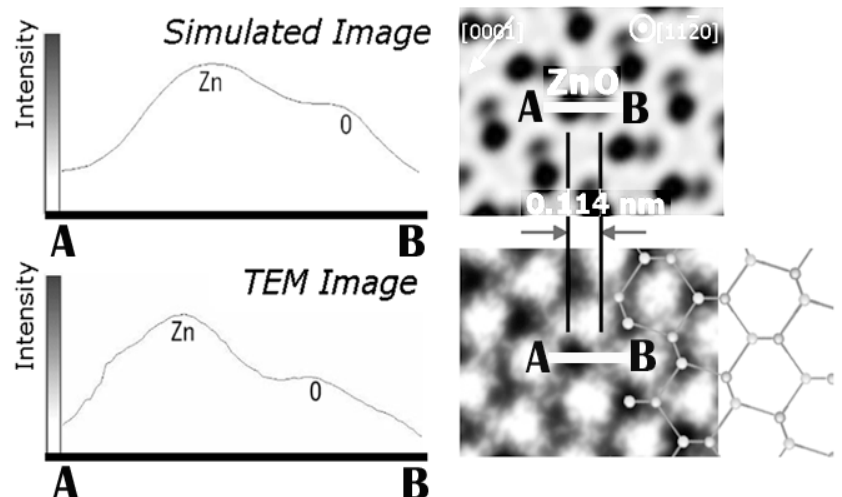


Fig.1. Identification of Zinc and Oxygen in the ARHVTEM atomic structure image. Zn appears in darker contrast and O in the thinner in both calculated image and picture. Projected inter atomic distance of Zn and O is 0.114nm.

Geometry of Pd/ZnO interface

The ZnO crystal and the Pd matrix were joined together by (0001) plane of the ZnO and (111) plane of the Pd. The (0001) plane is a polar interface stacked in turn by Zn-plane and O-plane. $\langle 110 \rangle$ axis of the Pd and $\langle 11\bar{2}0 \rangle$ axis of the ZnO were parallel to each other and to the electron beam too. (This interface is noted as ZnO(0001)/Pd(111) hereafter and is called as a polar interface.) Although most developed surface of a ZnO crystal grown in the free space is $(20\bar{2}1)$ plane, the (0001) plan exceedingly developed in the present ZnO crystal precipitated in the Pd matrix (Fig.2). 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.3).

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

Atomic arrangement shown by white dots in figure 3 is unusually straight everywhere in spite of 14% lattice mismatch at the interface. The 14% lattice mismatch, according to O-lattice model [4], must introduce a misfit dislocation at every eight (111) planes of Pd along the interface. 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 periodic image contrast of the misfit dislocation was seen (Fig.2.). No evidence of atomic site shift parallel to the interface, corresponding to the strain field of the misfit dislocation, was observed even in the lattice image of high resolution TEM; every white dot in figure 3 ranged straight directing to the interface. No strain localization around the misfit dislocation seems present. An absence of the periodic strain localization means that no stress accommodation mechanism works in the interface. Under this situation inter atomic distance across the interface changes from place to place. If the ZnO/Pd junction is exposed to cyclic heating, the uppermost inter atomic distance may go over the threshold of local atomic bonding by thermal strain due to different thermal expansion coefficient. Repeated the process by the cyclic heating a fine crack may grow to break all the interface atomic bonding.

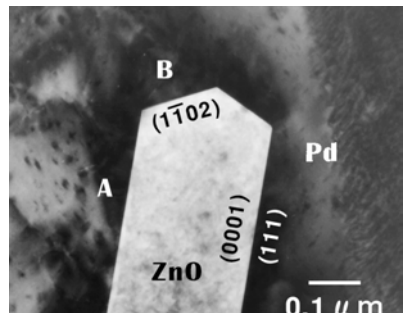


Fig.2. Well developed (0001) surface of ZnO.

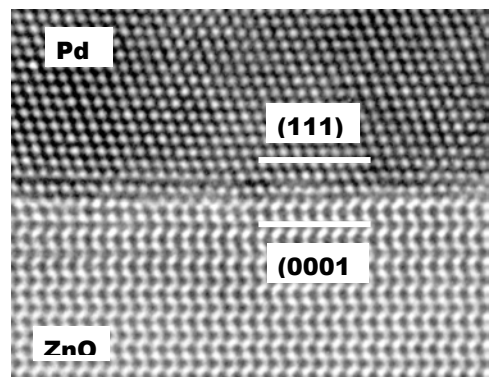


Fig.3. Well defined ZnO/Pd interface. Interface is parallel to (111) plane of Pd and (0001) plane of ZnO.

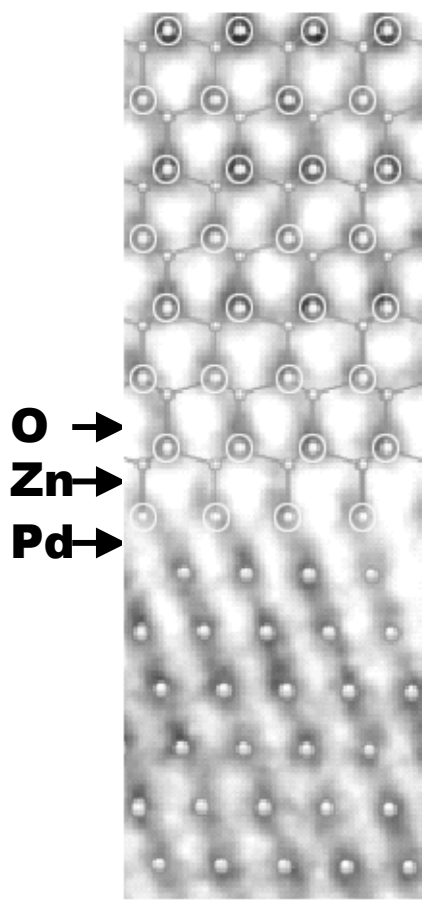


Fig.4. Well defined ZnO/Pd interface. Interface is parallel to (111) plane of Pd and (0001) plane of ZnO.

Chemical structure of the ZnO/Pd interface

Employed an atomic structure image which is observed under strict condition, namely less specimen thickness than 30nm, a super high resolution TEM with 0.1nm resolution, strict optical axis alignment, an obtained data (picture) will be capable of not only atomic structure analysis but also chemical structure investigation [4].

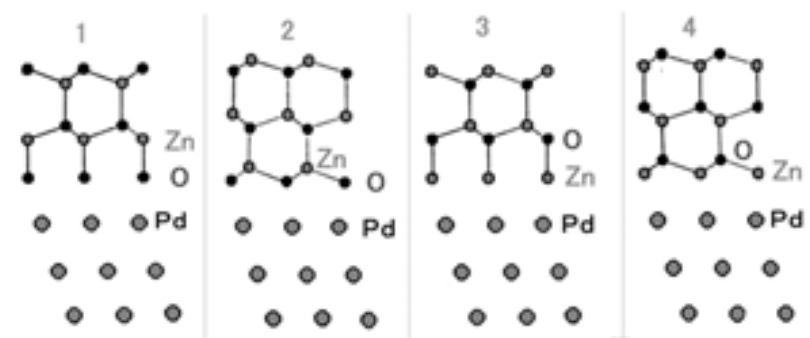


Fig.5. Four candidate structure models of the ZnO/Pd interface viewed from $\langle 11\bar{2}0 \rangle$ direction. #3 is the most likely structure.

Pictures shown in figure1 and figure 4 fulfill the required condition.

Chemical structure of the ZnO(0001)/Pd(111) interface was investigated by the image of figure 4 following the principle shown in figure 1. \odot was put at Zn position, a darker spot in the ZnO region of the picture. Small dot was put at O position, a brighter spot. Medium size dot was put at Pd position in the bottom half region. As a result of this procedure 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 geometrical candidates as shown in figure 5. Although Zn connects to Pd also in the model #4, geometrical structure does not coincide with the present picture. The model #1 and #2 are totally not the case.

Periodic interface structure

Atomic structure image (projected potential image) in the wider region was inspected in order to see further precise structure which was hidden in figure 3 (lattice image). Atomic site was successfully pointed out in most area but in some small region the image contrast was not clear. An extent of the un clear diffused region was at most several (111) planes of Pd in diameter (encircled by dotted line in figure 6). No other characteristic feature such as atomic site shift was detectable even 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.

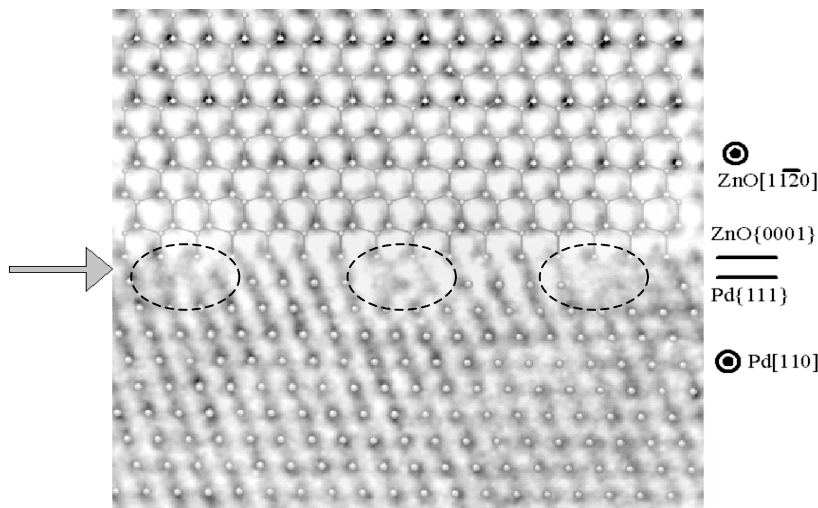
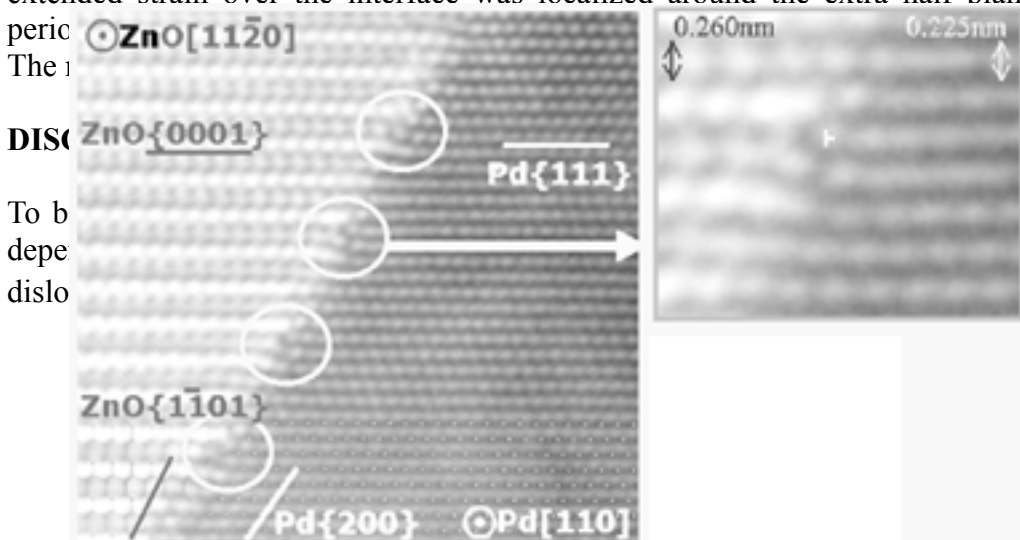


Fig.6. Atomic structure image of the ZnO/Pd junction. No local strain (stress) accommodation mechanism is recognized.

The diffused image in figure 6 is attributed to slight irregular atomic displacement. In this region, ordinary local atomic bonding may not be expected.

ZnO(1102)/Pd(200) non polar interface

A stress accommodation mechanism some times presented in the ZnO/Pd interface. In the case that the interface was parallel to (1101) plane of ZnO and (200) plane of Pd, periodic strain localization occurred (Fig.7(a)). An atomic arrangement of this structure is more apparent in the magnified image of encircled region of figure 7(a), shown in figure 7(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 diffused region coincided with that of misfit dislocation.



predicted by O-lattice model. mechanism.

To be dependent on the stress accommodation mechanism by the misfit localization in the ZnO(1101)/Pd(200) interface.

Fig.7. In the non polar interface parallel to $(1\bar{1}01)$ plane of ZnO and (200) plane of Pd periodic strain localization occurs.

interface (Fig.7). Geometrical parameter seems to control the interface structure. However, the geometry can not be an essential cause in the physical phenomena. Physical contents which is adjoined (is represented) by the geometrical parameter must be essential cause. In the present system heterogeneous 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 employing ARHVTEM in order to see the cause of weakness of a metal/ceramic bonding against cyclic heating. 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.

REFERENCES

- 1)W.Mader: Mat. Res. Soc. Symp. Proc. Vol82 (1987) 403,PLU and F.Cosandey;Acta.amet.Vol.40(1992)s259-266
T.Muschik and M.Ruhle; Phil.Mag.Vol.65(1992)263-388
- 2)H.Ichinose, H.Sawada, E.Takuma and M.Osaki: J.Electron Microscopy 48 (6) 887-891 (1999)
- 3)S.Horiuchi: High-resolution evaluation electron microscope, Kyoritsu Shuppan (1988)
- 4)W.Bollman: Crystal Defects and Crystalline Interfaces, Springer-Verlag (1980)