LATVIAN JOURNAL OF PHYSICS AND TECHNICAL SCIENCES
2005, N 1

SOLID STATE PHYSICS

EFFECT OF MECHANOACTIVATION ON INTERFACIAL INTERACTION IN METAL/OXIDE SYSTEMS

F. Muktepavela, G. Bakradze, V. Skvortsova

Institute of Solid State Physics, University of Latvia,
Kengaraga iela 8, Riga, LV1063, LATVIA

E. Tamanis

Daugavpils University,
Parades iela 1, Daugavpils, LV5400, LATVIA

S. Stolyarova

Technion, Solid State Institute,
Technion-City, Haifa 32000, ISRAEL

Properties of interfaces in solid state metal/oxide joints (Al/SiO_2, Al/MgO, Al/glass, Mg/MgO, Mg/SiO_2, In/glass etc) are reported. The interfaces were formed at plastic deformation of metal on the oxide surface at room temperature. Their structure, composition, and micromechanical properties were studied by the AFM, X-ray diffraction, SIMS, optical microscopy, and precision microindentation techniques. A noticeable adhesion was observed for metals with high affinity for oxygen and only in the regions of the maximum shear stress. Formation of a reaction zone with an oxygen concentration gradient in which the metal near interface hardens is detected. The effect of mechanoactivation is considered as a result of physical and chemical interaction and formation of nanostructures in deformed metal/oxide systems.

Keywords: *metal/oxide (metal/ceramic) interfaces, adhesion, mechanoactivation, micromechanical properties, nanostructure.*

1. INTRODUCTION

Metal/oxide interfaces play a crucial role in many important present-day technological applications such as optoelectronic and microelectronic systems, heterogeneous catalysis, oxide dispersion-strengthened alloys, powder materials, solid state joint devices, anticorrosion and thermal insulation coating industry, etc.; moreover, they have found important applications in medicine [1–3]. In such applications, often the properties of the heterophase interface, but not of the bulk materials, determine the behaviour of a system. Mechanical properties, structure, and adhesion strength on metal/oxide interfaces are of the greatest concern. Most of studies in this area have been performed at high temperatures and are devoted to the role of diffusion processes in the formation of the structure and adhesion bonds [2–5]. At the same time, comparatively little attention has been paid to the obtaining of metal-oxide composites at room temperature, when thermoactivation of adhesion is negligible. Only few sources of detailed information in literature on this problem provide evidence of such possibility [6–8]. According to some theoretical works [9, 10], it is possible to enhance the adhesion at metal/oxide interfaces at room temperature by introducing the structural defects into oxide surface layers.

The question about the role played by structural defects in the formation of a chemical bond at the solid-state interfaces is still controversial. On the one hand, there are considerations about active centres of adhesion such as dislocations and vacancy groups [11]. On the other, experimental data on atomically-clean metal/metal, metal/Si and metal/Ge interfaces have shown that under the conditions of full contact the atomic interaction occurs with formation of chemical bonds, and no further activation of the surfaces is needed [12–14]. In this case, the thermodynamical gain in surface energy (ΔF) of two fully contacting materials could be expressed as follows:

$$\Delta F = \gamma_o^A + \gamma_o^B - \gamma_{ib}^{AB},$$

where γ_o^A is the surface energy of the contacting metal A; γ_o^B is the surface energy of the contacting metal B (or semi-conductor); and γ_{ib}^{AB} is the interphase boundary energy. Evidently, the ΔF values for such systems as metal/metal, metal/Si and metal/Ge are high enough to form chemical bonding between the contacting surfaces. For the systems metal/oxide the influence of the oxide surface activation on the adhesion strength could be expected. One of the possible activation means is the mechanoactivation of oxide surface layers by plastic flow of metals. However, experimental data on metal/oxide solid state joining at room temperature are seldom met in the literature.

In the present work, the properties of interfaces in solid state joints of metal/oxide (Al/SiO_2, Al/MgO, In/glass, Mg/SiO_2, and others) formed by plastic flow of metals at room temperature are investigated.

2. EXPERIMENTAL PROCEDURE

The metal/oxide solid-state joints were obtained by static compression of freshly prepared metal and oxide surfaces at room temperature. The contact experiments with atomically-clean surfaces were performed in high vacuum (10^{-6} Pa) and in air by the controlled rupture/cleaving of the samples. Right after the rupture of samples the surfaces of metal and oxide were brought into contact with each other. The interfaces were formed under the conditions of plastic flow of metal on oxide surface. For our studies, polycrystalline simple metals (Al, Sn, Pb, Mg, Cd, In), boron-silica glass, and single crystal oxides (SiO_2, Al_2O_3, MgO) were chosen. The adhesion strengths of joints were determined in pull-off tests. The fracture mode was examined after the tests. The structure and composition of fracture surfaces were studied by optical microscopy (NEOPHOT 30), AFM (Nanoscope), X-ray diffraction (DRON-3M), and SIMS (Secondary Ion Mass Spectrometry). For the SIMS method, Ar^+ ions with energy of 6keV were used, the ion sputtering rate being 0.01–0.02 µm/min. The peak intensity (I^+, arbitrary units) of the investigated elements served as a working standard. The micromechanical properties were determined by a microhardness tester allowing the measurements to be carried out at very small loading ($3 \cdot 10^{-3}$ N) [15]. The indentor was a Vicker's diamond pyramid. To reveal the presence of dislocations in MgO single crystals the chemical etchant: 5 parts of saturated NH_4Cl solution, one part of H_2SO_4 and one part of distilled water – was used.

3. RESULTS AND DISCUSSION

The results of mechanical tests have shown that the metals Al, In and Mg have the strongest adhesion to the oxides (Table 1). Fractures of these joints occurred with the transfer of metal to the surface of oxide, being the evidence of a strong chemical bonding at the metal/oxide interfaces. The adhesion strength of Sn, Cd, Pb was much smaller than in the case of aluminium, indium or magnesium, and in many cases fractures occurred along the metal/oxide interfaces. The observed distinction in the adhesion strength between the investigated metals can be explained in terms of the thermodynamics of chemical interaction between metals and oxygen of the oxide.

Table 1

Adhesion strength (σ, MPa), transfer of metal (+ or –) to oxide surfaces in pull-off tests of metal/oxide joints, and metal oxide formation energies ($-\Delta Z_{293}\cdot 10^{-6}$, J/kmol)

Oxide / Metal	σ, MPa								Metal oxide	$\Delta Z_{293}\cdot 10^{-6}$, J/kmol
	Glass		SiO_2		Al_2O_3		MgO			
Al	60	+	62	+	65	+	60	+	Al_2O_3	1675
In	25	+	20	+	18	+	18	+	In_2O_3	926
Mg	22	+	15	+	20	+	25	+	MgO	602
Sn	2	+	10	+	0	–	10	+	SnO_2	581
Cd	2	–	0	–	5	+	5	+	CdO	260
Pb	2	–	2	+	0	–	5	–	PbO	219

Table 1 shows that the oxide formation energy increases from aluminium to lead. Metals with a high affinity for oxygen form stronger adhesive bonds with the surface of oxides. To verify this, more than one set of experiments were run. This result will be compared with the experimental data obtained by other authors who studied the adhesion on thin-film metals/oxide systems after the activation by electron or ion beam and in wetting experiments [16]. However, in our case the formation of strong adhesion in these systems occurs not over the whole contact area but only in the regions of the maximum shear stress (Fig.1, *a*).

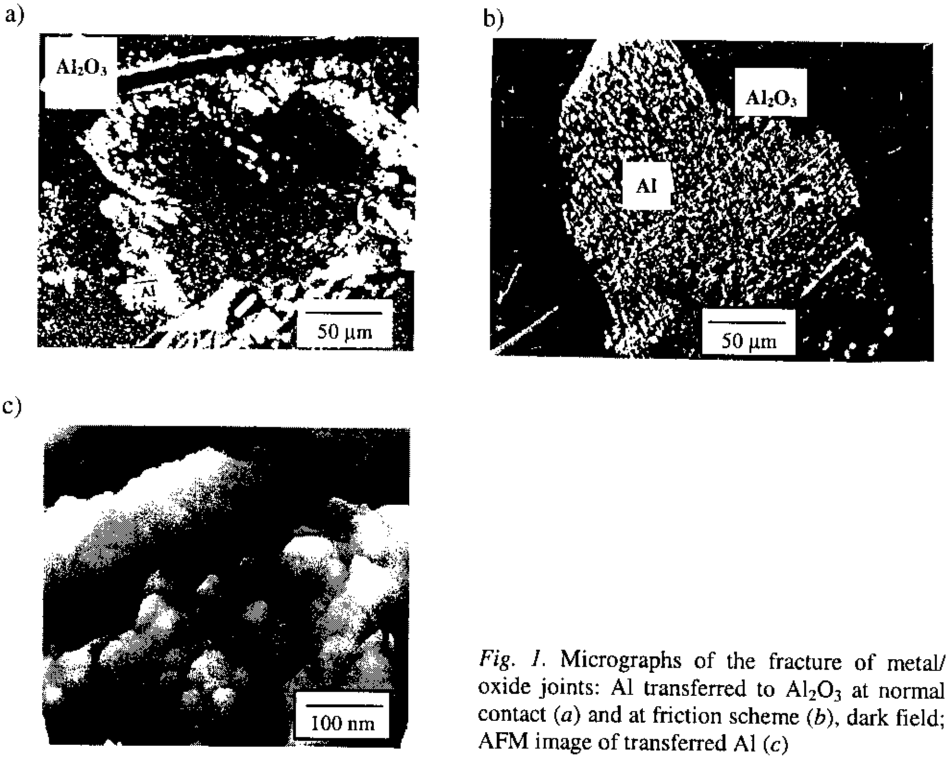

Fig. 1. Micrographs of the fracture of metal/oxide joints: Al transferred to Al_2O_3 at normal contact (*a*) and at friction scheme (*b*), dark field; AFM image of transferred Al (*c*)

Special experiments with the Al/glass system were performed so that plastic flow of Al on the surface of glass could be obtained under friction. In this case strong adhesion is observed over the whole surface of oxide (Fig.1, *b*). The AFM studies of surfaces show that the transferred metals (Al in this case) have a nanostructure with a grain size from 30 to 100 nm (Fig.1, *c*), though the nanostructure is not homogeneous. This result was confirmed by our X-ray diffraction data and, in addition, it shows that the nanostructure of the transferred Al is stable after annealing in vacuum. Thus, the action of the maximum shear stress leads to the formation of nanostructure in metal near the interface. The raised density of defects on the grain boundaries characterizes this strongly deformed state of metal. It could be assumed that the metals with high affinity for oxygen and having nanostructured state form chemical bonds with the oxides more easily.

If we consider the obtained result for some processes on the oxide surface, we can explain the metal/oxide chemical bonding at room temperature by mechanoactivation of the oxide surface. Also, the possibility exists of such mechanoactivation by plastic flow of metal. Point defects and dislocations may be treated as the main influencing structural factors. The energy of point defect formation in oxide is insignificant (≈ 2 eV). Therefore, it is possible to assume with confidence that point defects are formed in the near-surface layers of oxide even at room temperature under the active plastic flow of all investigated metals. On the other hand, it was interesting to find out the role of dislocations of oxide in the formation of adhesive bonds. If dislocations in the zones of metal transfer to the oxide cause the occurrence of adhesive bonds, then by etching it would be possible to reveal this. We have studied the role of dislocations in In/MgO and Pb/MgO systems, with different (as shown above in Table 1) adhesion and thermodynamics of metal/oxygen interaction (e.g indium showed strong adhesion to a crystal, with transfer of metal to the MgO surface at the testing of joints). At the same time, adhesion of lead did not exceed the level of physical adsorption, and no transfer of metal was observed. Except for that, the hardness of soft In (about 16 MPa) was smaller than the value of starting stress for dislocations in MgO ($\tau_0 \approx$ 28–30 MPa), whereas the hardness of Pb (30 MPa) should be sufficient to create fresh dislocations in MgO [17]. Etching experiments on the MgO crystal did not reveal the presence of new dislocations around and inside the area of the transferred In (Fig. 2, *a*). As concerns lead, groups of fresh dislocations are clearly visible in the field of its contact with the crystal in the area of the maximum shear stress in MgO, but without any trace of Pb adhesion with MgO (Fig. 2, *b*). So, at present there is sufficient evidence that dislocations do not play any significant role in the formation of chemical bonding between metal/oxide interfaces. Apparently, the high concentration of point defects on oxide surface can be the primary mechanoactivation factor of adhesion with metals. We can assume that the presence of point defects facilitates the formation of metal-oxygen complex.

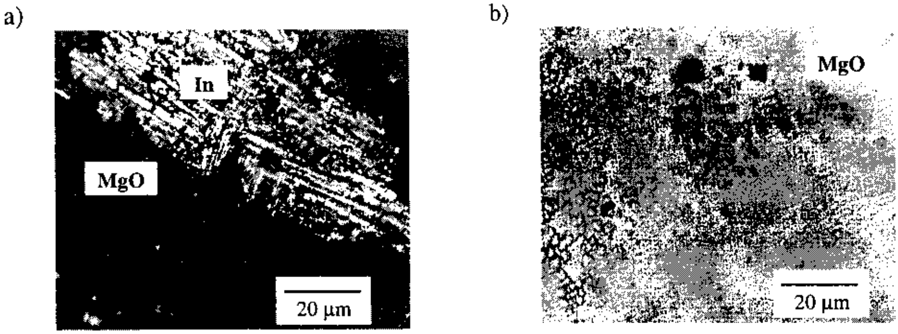

Fig. 2. Micrographs of the etched MgO surface after contact with In (*a*) and Pb (*b*)

The leading role of oxygen and point defects in the formation of metal/oxide adhesion is confirmed by the theoretical data on adsorption and by the experimental data on thin film adhesion in metal/oxide systems [9, 10, 18]. To verify this hypothesis in our case the chemical compound of the metal transferred to oxide was experimentally traced level-by-level by the SIMS method. Here, as an example, the result obtained for aluminium transferred to glass is given in Fig. 3, which shows the presence of oxidized aluminium. This result testifies about the formation of a reaction Me-MeO zone (with a size of 0.5–1 μm) spreading in the metal, with a gradient of oxygen concentration. The formation of such a zone is possible only for metals with a high activity to oxygen and also because of many deformation defects and the nanostructure of metals. The grain boundary diffusion coefficients in nanomaterials synthesized by means of severe plastic deformation are known to be an order of magnitude higher than in classical polycrystals [19, 20].

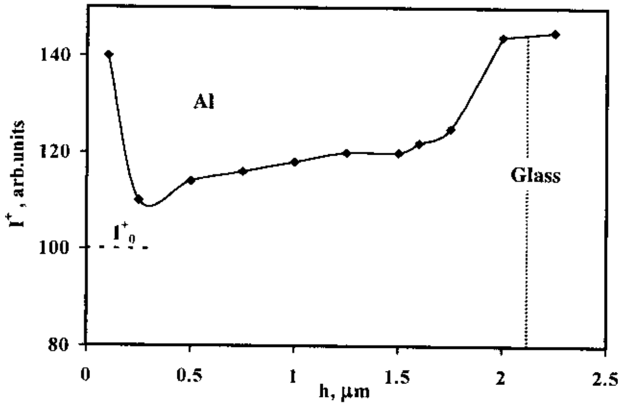

Fig. 3. Depth profile of the intensity of SIMS-signal of Al^+ in the Al transferred to glass. The intensity of non-oxidized Al is pointed as I^+_0

Thus, in the regions of maximum shear stress the processes of atomic diffusion of oxygen and formation of metal-oxygen complexes can take place. In turn, a change in the mechanical properties of metals near the interface can also be expected. The presence of metal oxide – even nonstoichiometric one – should raise the hardness of metals. We can compare the mechanical properties of metals on the fracture surfaces at metal/oxide joints with those of deformed bulk metals. The data on Al and In are presented in Table 2. As is seen, the microhardness of the two metals noticeably increases in the fracture zone. At the same time, the strength value for aluminium decreases, while in the case of indium it remains high. Apparently, a brittle Al–Al_xO_y composite forms at Al/oxide interface (Al_2O_3 is known to be a very hard and brittle material). For In_2O_3 these properties are expressed weaker, and formation of such oxide causes increase both in hardness and in strength.

Table 2

Microhardness (*H*, MPa) and strength (σ, MPa) of the deformed bulk metals and the metals transferred to SiO_2

Metal	*H*, MPa		σ, MPa	
	bulk metal	tansferred metal	bulk metal	transferred metal
Al	400	700	200	62
In	16	150	9	15

The change in mechanical properties of metal near the metal/oxide interface corresponds to the SIMS data and testifies about the formation of a reaction zone under influence of plastic deformation.

4. CONCLUSIONS

The investigation carried out by us allows the conclusion to be drawn that a strong chemical adhesion arises on the metal/oxide interface under plastic deformation of metal at room temperature. Mechanoactivation of the adhesion occurs in the metals with low oxide formation energies only in the regions of the maximum shear stress. In such regions the metals are nanostructured and noticeably hardened. Influence of dislocations on the oxide surface was found to be insignificant; at the same time, the nanostructural state of metal, together with the high concentration of point defects in the near-surface layer of oxide, can be the primary factors of interfacial chemical interaction in metal/oxide systems.

REFERENCES

1. Ernst F. (1995) Metal-oxide interfaces *J. Mat. Sci. Eng.* **R14** 97–156.
2. Lojkowski W., Fecht H.-J. (2000) *The Structure of Intercrystalline Interfaces* Progress in Materials Science **45** :Pergamon, 339–568.
3. Sinnott S.B., Dickey E.C. (2003) Ceramic/metal interface structures and their relationship to atomic-and meso-scale properties *Mater. Sci. Eng. R-Reports* **R43** 1–59.
4. Wagner M., Wagner T., Caroll D.L., Marien J., Bonnell D.A., and Rühle M. (1997) *Model Systems for Metal-Ceramic Interface Studies* MRS Bulletin **22** 8-15.
5. Akatsu T., Hosoda N., Suga T., Rühle M. (1999) Microstructure of Al/α-Al_2O_3 interface fabricated by surface activated bonding at room temperature *Mat. Sci. Forum* **329** 294–297.
6. Keino M., Shinichiro F. (1991) Microstructure and adhesion mechanism of mechanically prepared composite particles *J. Mater. Sci. Eng. B* **10** 139–147.
7. Muktepavela F., Manika I., Kalnacs J. (2000) Investigation of mechanically alloyed metal/oxide coatings by SIMS method *Latv. J. Phys. Tech . Sci.* **6** 141–144.
8. Bailey F.P., .Black K.J.T (1978) Au/Al_2O_3 solid state reaction *J. Mat. Sci.* **13**, 1045–1050.
9. Zhukovskii Yu.F., Kotomin E.A., Jacobs P.W.M., Stoneham A.M., Harding J.H. (2000) Modelling of silver adhesion on MgO(100) surface with defects *J. Phys. Condens. Matter.* **12** 55–66.
10. Duffy D., Harding J. and Stoneham A.M. (1994) The energies of point defects near metal/oxide interfaces *J. Appl. Phys.* **76** 2791–2798.
11. Krasulin Ju. L.(1971) *Interaction of Metal with Semiconductor in Solid State* Moscow: Nauka (in Russian).
12. Upit G.P. (1971) Bonding of juvenile surfaces of Al with Si. *Izvestija AN Latv. PSR ser. phys-tech. nauk* **1** 22–25 (in Russian).
13. Muktepavela F., Maniks J. (1998) Mechanical properties and accommodation processes on metallic interfaces *Nanostructured Materials* **10** (3) 479–484.
14. Buckley D.H. (1981) *Surface Effects in Adhesion Friction, Wear and Lubrication* Amsterdam: Elsevier.
15. Muktepavela F., Manika I., Mironovs V. (1997) Structure and mechanical properties of Al–B composite powder *Mat.Design* **18** 257–259.
16. Woirgard J., Cabioc T., Riviere J.P., Dargenton J.C. (1998) Nanoindentation characterization of SiC coatings prepared by dynamic ion mixing *Surf.&Coat. Techn.* **100–101** 128–131.
17. Sangwal K., Sanz F., Gorostiza P. (1999) Study of the surface morphology of the (100) cleavage planes of MgO single crystals by atomic force microscopy *Surf. Sci.* **424** 139–144.
18. Netzer F.P (2002) Interfacial oxide layers at the metal-oxide phase boundary *Surf. Rev. &Let.* **9** 1553–1563.

19. Paritskaya L.N., Kaganovskii Yu., Bogdanov V.V. (2005) Size-dependent interdiffusion in nanomaterials *Sol. St. Phen.* **101–102** 123–130.
20. Valiev R.Z., Alexandrov I.V., Islamgaliev R.K. (1998) Processing and properties of nanostructured materials prepared by severe plastic deformation (ed. Chow G.M., Noskova N.I.) *Nanostructured materials* NATO ASI series **50** 121–142.

MEHĀNOAKTIVĀCIJAS IETEKME UZ METĀLA/OKSĪDA ROBEŽVIRSMAS MIJIEDARBĪBU

F. Muktepāvela, G. Bakradze, V. Skvorcova, E. Tamanis, S. Stoļarova

Kopsavilkums

Pētīti metāla/oksīda (Al/SiO_2, In/MgO, Pb/MgO, Mg/SiO_2, Al/Al_2O_3 uc) robežvirsmu adhēzijas procesi un mehāniskās īpašības. Metālu cietfāžu savienojumi ar oksīdiem tika iegūti aukstās metāla plastiskās deformācijas apstākļos. Tika izmantotas SIMS, AFM, X-ray optiskās un elektronu mikroskopijas un precīzās mikrocietības metodes. Atrasts, ka ievērojamā adhēzija notiek tikai bīdes deformāciju zonās, un tā vērojama sistēmām, kuras raksturojas ar augstu metāla radniecību ar skābekli. Uz robežvirsmas no metāla puses veidojas reakcijas zona, kas raksturojas ar nanostruktūru, skābekļa koncentrācijas gradientu un paaugstinātu mikrocietību. Mehānoaktivācijas ietekme tika izskatīta kā punktveida defektu izveidošanas oksīda virsmas slānī, struktūras pārvērtības metālā un ķīmisko reakciju rezultāts.

06.01.2005.