Available online at www.sciencedirect.com
SCIENCE DIRECT®
Scripta Materialia 54 (2006) 453–457
Scripta MATERIALIA
www.actamat-journals.com

Adhesion strength of Ag/BaTiO$_3$ interface

Chao-Yu Lee [a,b,*], Michel Dupeux [b], Wei-Hsing Tuan [a]

[a] Department of Materials Science and Engineering, National Taiwan University, 1 Roosevelt Road, Sec. 4, Taipei 10617, Taiwan, ROC
[b] Laboratoire de Thermodynamique et Physico-Chimie Métallurgiques (LTPCM), Universite Joseph Fourier, France

Received 24 May 2005; received in revised form 29 September 2005; accepted 8 October 2005
Available online 2 November 2005

Abstract

The adhesion strength between a silver electrode and pure barium titanate has been determined by using a blister test. The Ag electrode is a porous layer and the barium titanate substrate is dense. The critical interface crack propagation energy G_{ci} of the Ag/BaTiO$_3$ interface ranges between 1.3 J/m^2 and 4.2 J/m^2.

Keywords: Interface; Adhesion; Ag electrode; Barium titanate

1. Introduction

The characteristics of metal–ceramic interfaces play an important role in many applications, such as electronic packages, multilayer ceramic capacitors (MLCC), wear resistant coatings, thermal barrier coatings, micro-electro-mechanical systems etc. The interfacial strength is an important parameter for all applications. Many different methods have been proposed to measure the adhesion strength of the metal–oxide interface [1]. These methods, however, are very specific and often their results are mutually inconsistent. Furthermore, most methods fail to deliver quantitative results with physical meaning.

The blister test is one of the few methods which can deliver quantitative and meaningful estimation on interfacial strength through the determination of the critical interfacial crack propagation energy. For the test, a rigid substrate with a hole located at the center of the substrate is needed. The substrate, including the hole, is then covered with the film. During the blister testing, the pressure applied to the film through the hole is augmented until the film begins to debond from the substrate. The blister shape before and after debonding is demonstrated in Fig. 1. After the bulging of the self-standing part of the film that covers the hole, a circular blister is formed and grows steadily in diameter. The critical strain energy release rate of the interface crack is determined from the height of blister and the pressure applied during crack growth.

Blister tests are simple and straightforward to analyse only when there is no generalized film yielding before debonding. Another limit of the test is that the crack has to propagate uniformly along the perimeter of the blister. Although the blister test has several limits, it is a reliable method to determine the amount of energy required to debond the film from its substrate, a quantity which characterizes the film adhesion.

The blister test as a standard method for measuring the adhesive strength of thin coatings was first suggested by Dannenberg [2]. The crack propagation energy G_{ci} is calculated directly from the pressure (P_c) vs. volume change (ΔV). The strain energy of the pressurized film is the amount of work required to inflate the film from an initially flat state to a height h, as

$$U_{\text{strain}} = \int_0^h p(h)\,\mathrm{d}V \qquad (1)$$

---

[*] Corresponding author. Address: Department of Materials Science and Engineering, National Taiwan University, 1 Roosevelt Road, Sec. 4, Taipei 10617, Taiwan, ROC. Tel.: +886 2 23659794; fax: +886 2 23634562.
E-mail address: cohesivelee@yahoo.com.tw (C.-Y. Lee).

1359-6462/$ - see front matter © 2005 Acta Materialia Inc. Published by Elsevier Ltd. All rights reserved.
doi:10.1016/j.scriptamat.2005.10.020

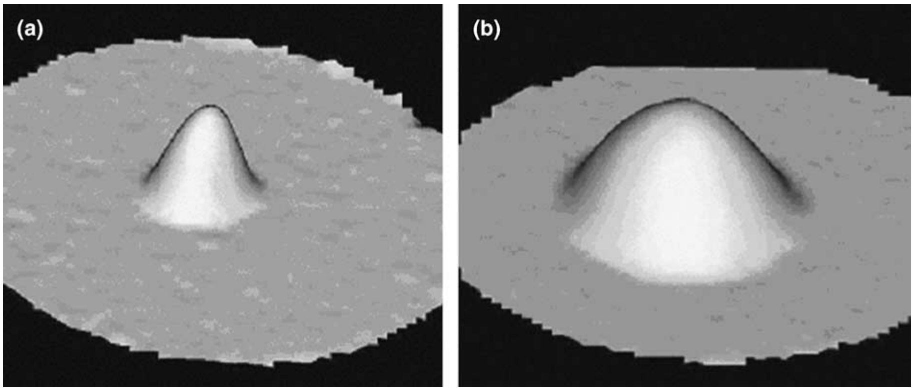

Fig. 1. 3-D-profilometry reconstruction of the Ag electrode: (a) before debonding (the Ag membrane bulge diameter is restricted to the hole) and (b) after debonding during the blister test (blister heights are strongly amplified by 3-D imaging).

The work done on the film by the applied pressure while the blister with radius a growing is

$$\frac{\partial W_{\text{ext}}}{\partial a}=\frac{\partial (pV)}{\partial a} \tag{2}$$

The expression for G can then be approximated as [3]

$$G = C \cdot p \cdot h \tag{3}$$

where C is a dimensionless constant which is a function of the residual stress σ_0 in film, of film biaxial modulus $E/(1-\nu)$ and of the geometrical ratio h/a. As the blister is forming, the equilibrium shape of the blister contour is circular and its ratio h/a is almost constant. The value of C can be taken as a constant during the test; this value is 0.516 for the case of high residual stresses and 0.645 for the case of low residual stresses [3,4].

2. Experimental procedures

A barium titanate powder (Product No. 219-6, Ferro Co., USA) was used in the present study. The purity of the $BaTiO_3$ powder was higher than 99.6%. A disc with a diameter of 25 mm and thickness of 2.5 mm was prepared by die-pressing at 60 MPa. The disc was first pre-fired at 1190 °C for 1 h to obtain a handling strength. A hole with a diameter of 2 mm was then machined into the center of the pre-fired disc by using a steel drill. The disc was then sintered at 1290 °C for 2 h. The relative density of $BaTiO_3$ was then >95%. Finally the disks were ground with fine SiC particles to achieve a flat smooth surface.

A silver paste (Ag 8985, Shoei Co., Japan) composed of silver particles, binder and a small amount of glass particles was used. Screen printing was used to apply the Ag paste onto the flat surface of the $BaTiO_3$ disc. Before screen printing, an adhesive tape patch was applied to cover the central hole of the disc. The $BaTiO_3$ discs with this printed first Ag layer were fired at 600 °C for 1 h to remove the adhesive tape. The discs with electrode including the free-standing membrane over the hole were then screen printed and fired several times until the desired thickness of Ag layer was achieved.

The apparatus used for the blister test consisted of a quadrilateral metal block specimen holder and pressurizing stage, and an optical measurement equipment. A fringe projection device was used to measure the vertical displacement of the specimen surface during the blister test [5]. The test sample was mounted on the top of the blister pressurizing stage. An expanded set of parallel fringes, produced by the interference of two laser beams, was projected under a certain angle on the top of the sample. A CCD camera was fixed above the blister apparatus to photograph the top view of the fringes on the specimen surface, which was then analyzed by a computer. Commercial software (HOLO 3: Fringe Analysis®) was used to analyze the results. The setup of the facilities is illustrated in Fig. 2.

The elastic modulus of porous Ag electrode before and after blister test was determined by using a nanoindenter (XP, MTS, USA). The specimen cross-sectional microstructure was observed by scanning electron microscopy (SEM) on samples before and after the blister test.

3. Results and discussion

The cross-section of a specimen after sintering is shown in Fig. 3. The $Ag/BaTiO_3$ interface is relatively smooth. The free-standing Ag electrode is porous. The relative density of the Ag electrode, as estimated by using image analysis, is around 73%. This density is slightly higher near the interface due to the fact that the electrode near the interface has been fired several times. The thickness of the silver electrode has been changed by between 80 μm and 170 μm. The thickness was measured by a micrometer, with reference to the initial substrate thickness. Five points have been measured and the average was taken as film thickness. Because the pores within the Ag electrode are interconnected, while the film is pressurized by distilled water, water could penetrate through the electrode. Therefore, an adhesive film (about 10 μm) is applied to cover the electrode to make it waterproof. This layer is visible on the top of the electrode, Fig. 3. The influence of this adhesive film is negligible on the $Ag/BaTiO_3$ interfacial strength as long as it is attached firmly to the electrode throughout the blister test.

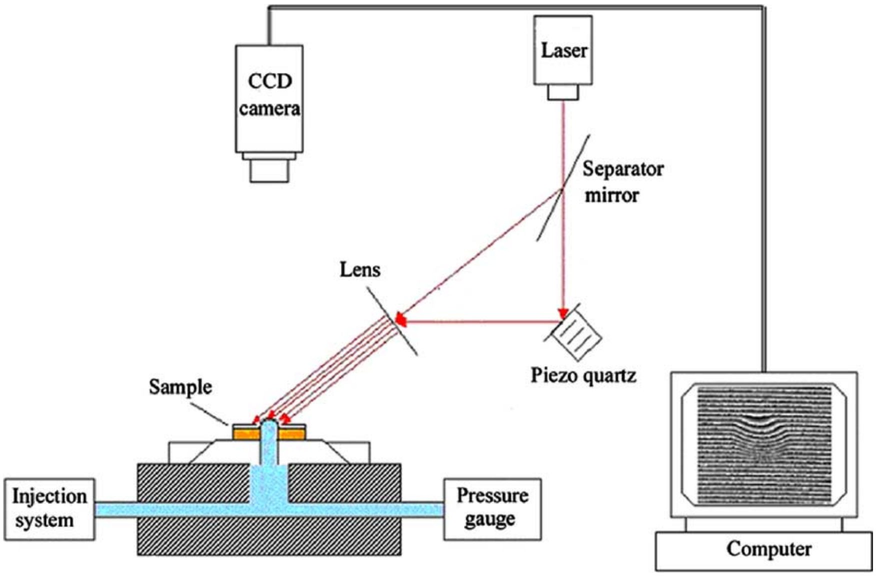

Fig. 2. Illustration of the complete blister test system.

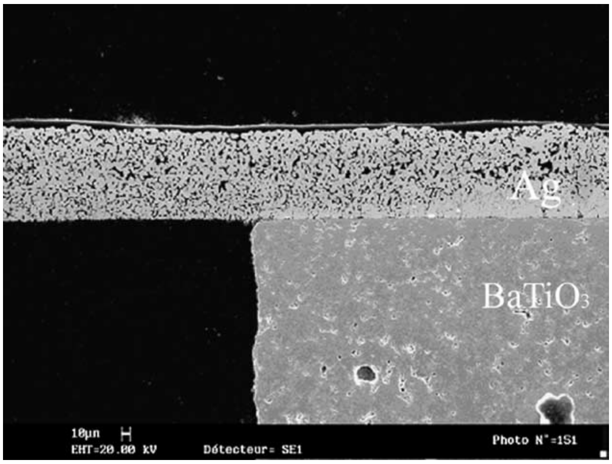

Fig. 3. Partial view of the cross-section of a non-deformed specimen.

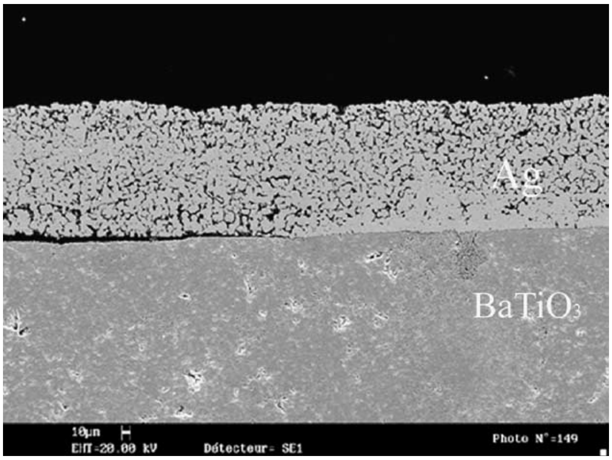

Fig. 4. Cross-sectional view of the crack-tip zone after the blister test.

Fig. 4 shows the crack-tip region at the electrode/substrate interface on the cross-section of a blister tested specimen. The fracture is mainly adhesive in nature at the observation scale of SEM. Evidence for plastic deformation can only be found at the crack tip. Near the crack tip, some pores appear to grow and coalesce with each other. Consequently some large pores are found at the interface on the silver side after debonding.

A nanoindentation test was used to determine the Young's modulus of the porous silver electrode. The average Young's modulus of the silver electrode before the blister test was 40 GPa, and after the blister test 20 GPa. The elastic modulus of bulk silver reported from literature is 76 GPa [6]. The porous structure and its modification by the plastic deformation [7,8] are the main reasons for this difference.

For other thin-film-on-substrate systems, it is usually assumed that the top film deforms elastically. Because of its thickness, porous structure and annealed microstructure, our silver electrode layer tends to deform plastically. Then the strain energy during blister test is composed of the work of elastic deformation and of plastic deformation.

At the beginning of the test, hydraulic pressure is applied to make the electrode layer blister and separate from substrate. Then the pressure is released and the p vs. h curve generally shows a residual deflection, proving that the film has been plastically deformed, because the stress and strain in the porous film have reached values beyond the porous film elastic limit. As long as the system is stable we repressurize to make blistering occur again and then release pressure. Each repeated pressurization can be used to determine the adhesion energy of the interface through Eq. (3). Therefore, we can obtain several results on one specimen until the electrode is broken or totally debonded.

Since the film has deformed plastically after previous pressurization, the volume underneath the new free-standing membrane can be related to its new radius a_p and plastic residual deflection height h_p, which will influence the result of the next blister test. The strain energy of the pressurized electrode film should then be changed to

$$U_{\text{strain}} = \int_{h_p}^{h_p+h} p(h)\,\mathrm{d}V \tag{4}$$

The part contributed by the plastic deformation should be extracted from the apparent energy release rate G at the interface crack, since only the elastic energy stored in the membrane is available to be released and to contribute to crack propagation.

To determine the interface strength we need to fit the blister Eq. (3) to the experimental data corresponding to successive critical debonding points on the p vs. h curve. Usually the experimental value, h_{exp}, is fitted directly as the height to obtain G_c. In the present case the height of deflection contributed by plastic deformation h_{pla} (determined from the residual deflection after pressure release) should be removed from the experimental total value, h_{exp}. The height of deflection is corrected as $h = h_{\text{exp}} - h_{\text{pla}}$ when we fit the blister equation to the experimental data for debonding points. Thanks to this very simple procedure, we can subtract the effect of the generalized plastic yielding in the Ag membrane on the total strain energy produced by the application of pressure.

At each pressurization, since we record successive 3-D contours of the complete blister, we could check the diameter values to determine as accurately as possible when the blister begins to grow and the interfacial crack begins to propagate. We defined this point as the critical point to be used for G_c determination. Since the Ag membrane behaviour is dominated by residual stress (due to thermal contraction mismatch between metal and ceramic after firing) rather than by high Young's modulus and stiffness, we used $C = 0.516$ in Eq. (3) for the analysis of results in this study [3,4].

The resulting critical energy release rates G_{ci} of the $BaTiO_3$/Ag interfaces for each specimen are listed in Table 1. As explained before, these values are corrected by removing the influence of plastic deformation. The values of G_{ci} vary from 1.3 to 4.2 J/m^2, with an overall average value around 2.5 J/m^2. Besides intrinsic scattering of the adhesion from one specimen to another, the main contribution to the uncertainty may be attributed to the difficulty in determining the exact critical debonding points and subtracting the plastic strain contribution.

Very few values of interfacial crack propagation energies are available in the literature to compare with our results. Anyway, our values are higher than the usual estimates of the thermodynamic work of adhesion of metal/ceramic interfaces of around 1 J/m^2, while strongly adherent systems (like metal/metal or metal/adhesive interfaces) may reach interfacial crack propagation energies as high as hundreds of J/m^2 [9,10]. Thus the order of magnitude of the obtained values appears quite consistent with a reasonably strong metal/ceramic interfacial system, compatible with practical use in MLCCs.

One should also note that the adhesion strength is strongly affected by interfacial chemistry and cleanness, contact surface roughness (thus possibly the manufacturing process), the mode of loading and the activity of energy-dissipating processes such as plasticity or micro-cracks in either material. Although it will be interesting to cross-check these first results with other adhesion measurement techniques in the future, the loading mode mixity sensitivity will undoubtedly complicate this comparison.

More experiments with better accuracy and a wider range of electrode membrane thicknesses will be necessary to clear up these points.

4. Conclusions

Experimental data on the adhesion of metal/ceramic interfaces are few in the literature, especially for systems of direct interest for electrical or electronic applications [10]. Specimens typical of MLCC with a porous Ag electrode layer covering a dense $BaTiO_3$ substrate have been prepared with a special geometry appropriate for blister testing. The blister test technique allows for numerical estimation of interfacial adhesion strength through determination of the interfacial crack propagation energy. Simple methods are proposed to overcome experimental difficulties such as the porosity of the Ag layer or generalized plastic straining of this layer. With these blister tests, the critical interface crack propagation energy of the porous Ag/$BaTiO_3$ interface has been measured for the first time. Its average value is around 2.5 J/m^2. The technique which has been set up here is expected to be useful for more

Table 1
The critical interfacial energy release rates G_{ci} of Ag/$BaTiO_3$ interfaces

G_c of successive pressurizations	Sample no.								
	1	2	3	4	5	6	7	8	9
G_{c1} (J/m^2)	3.0	4.0	4.0		1.0	1.0	2.0	2.5	1.0
G_{c2} (J/m^2)	3.0	5.0	4.0		2.0	3.0		2.0	2.0
G_{c3} (J/m2)	5.0	3.0	4.0	5.0	1.0	1.0		2.0	
G_{c4} (J/m^2)	3.0		5.0	3.5					
G_{c5} (J/m^2)			3.0						
Average	3.5	4.0	4.0	4.2	1.3	1.7	2.0	2.2	1.5
Thickness (μm)	79	167	141	124	120	121	104	152	115

detailed exploration of the effect of various parameters governing metal/ceramic interfacial adhesion.

Acknowledgements

The present study was supported by the National Science Council, Taiwan, through the contract number of NSC94-2216-E-002-008 and Centre National de la Recherche Scientifique, France. The practical and financial help from the Institut Français de Taipei to C.Y. Lee and to the student exchange program between National Taiwan University, Taipei, and Université Joseph Fourier, Grenoble, is highly appreciated. The authors are grateful to Drs. M. Braccini and M. Verdier (LTPCM) for their help in nanoindentation hardness and modulus measurements.

References

[1] Ernst F. Mater Sci Eng R 1995;14:97.
[2] Dannenberg H. J Appl Polym Sci 1961;5:125.
[3] Hohlfelder RJ, Luo H, Vlassak JJ, Chidsey CED, Nix WD. Mater Res Soc Symp Proc 1997;436:115.
[4] Dupeux M, Bosseboeuf A. Interfacial science in ceramic joining. Boston, (MA): Kluwer Academic; 1998. p. 319.
[5] Mougin J, Dupeux M, Galerie A, Antoni L. Mater Sci Technol 2002;18:1217.
[6] Lerner LS. Physics for scientists and engineers. Boston, (MA): Jones and Bartlett; 1997.
[7] Roberts AP, Garboczi EJ. J Am Ceram Soc 2000;83:3041.
[8] Straffelini G, Molinari A. Mater Sci Eng 2002;334:96.
[9] Felder E, Darque-Ceretti E. Adhésion et Adhérence. CNRS; 2003.
[10] Volinsky AA, Moody NR, Gerberich WW. Acta Mater 2002;50:441.