FRACTURE TOUGHNESS OF NIOBIUM/SAPPHIRE INTERFACES: EFFECT OF INTERFACE DOPING AND ION ASSISTED DEPOSITION

G. S. Was[1] and H. Ji[2]

[1]Departments of Nuclear Engineering and Radiological Sciences, and Materials Science and Engineering, University of Michigan, Ann Arbor, MI 48109, USA
[2]Optoelectronics Division, Agere Systems, Reading, PA 19612, USA

ABSTRACT

In this work, the effect of chemical composition and crystal orientation relationship on the interface fracture toughness of niobium/sapphire system was studied. We used several techniques to assess the interface fracture toughness, including microscratch, microwedge scratch, and delamination of patterned lines. Results showed a general trend of the effect of silver at the interface where the interface fracture toughness decreased with the amount of silver. Ion bombardment during film deposition (IBAD) significantly increased the interface fracture toughness through a combination of interface mixing and a controlled orientation relationship.

KEYWORDS

Niobium, interface fracture toughness, delamination, ion bombardment, films, microwedge, microscratch

INTRODUCTION

The overall objective of this project was to control the fracture toughness of the interface between niobium films and sapphire substrates by controlling the interface properties. Scratch tests have shown [1] that the interface fracture toughness correlates with silver interlayer thickness for niobium films deposited by electron beam evaporation. It has also been shown [2] that ion bombardment during film deposition can be used to strengthen the interface by matching the crystal orientation across the interface and by interface mixing. Therefore, the approach used in this project involved both weakening the interface by doping it with silver [3,4] and strengthening it by controlling the orientation relationship and the degree of interface mixing.

Quantitative techniques for measuring interface fracture toughness in thin films are not well developed. In this paper, we have deduced values of interface fracture toughness using observations of failures that occurred during microscratching, microwedge scratching and from an analysis of bucking and curling of patterned niobium lines on sapphire. We were also able to assess the effectiveness of simultaneous ion bombardment during film deposition on the interface fracture toughness.

RESULTS AND DISCUSSION

Microscratch Experiments
Four sets of samples were made where a set constituted a series of depositions with varying interface silver level. All the films have a thickness of about 100 nm, as measured by the Dektak3 profilometer. The amount of silver at the niobium/sapphire interface varies from less than 0.8 monolayers to 6.4 monolayers as measured by RBS. Details of the experiment are given in ref. [5]. All samples with measurable silver level (>0.8 monolayer) at the interface failed during the scratch test with the niobium films delaminating from the sapphire substrates in a "brittle manner". The failure was characterized by multiple spallations as the film detached from the substrate (Fig. 1a). Buckling was also observed along the scratch track in areas prior to the first spall. The tangential load shows abrupt changes corresponding to the spalls and the breakthroughs of pile-up material in front of the indenter. Interfacial toughness can be obtained from the geometry of the first spallation and the tangential load at which it happened. On the other hand, there was no indication of interfacial failure during the scratch test for the sample with <0.8 monolayer of silver at the interface, as well as the sample without silver . The film underwent ploughing with no evidence of delamination (Fig. 1b). No value of interface fracture toughness was estimated for these two samples because of the absence of interfacial failure.

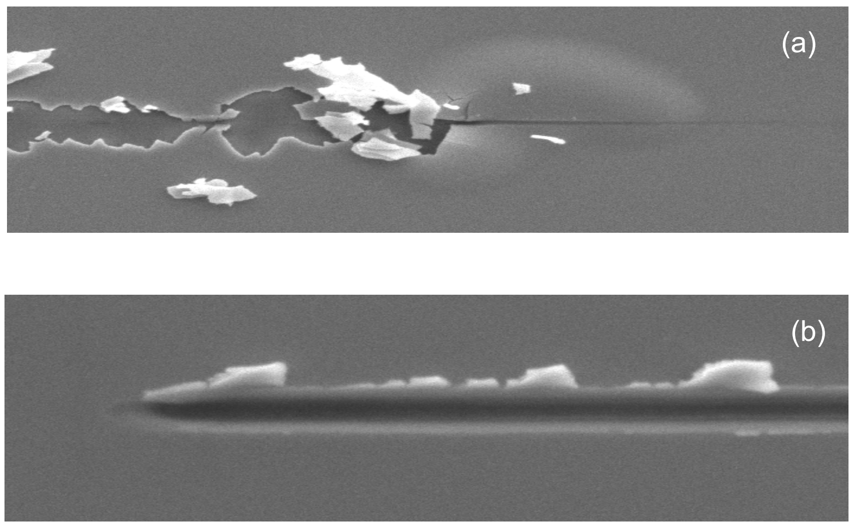


Figure 1: SEM micrographs of scratch tracks for (a) sample with interface delamination (PVD, 4.2 monolayers of silver), and (b) sample without interface delamination (PVD, < 0.8 monolayers of silver).

The results from microscratch test showed a strong correlation between the interface fracture toughness and the amount of silver at the interface, as plotted in Fig. 2a. This result is in good agreement with the general trend of the interface fracture toughness as a function of the work of adhesion. As been pointed out by Elssner *et al*. [2], the interface fracture toughness G_c, increases exponentially with the work of adhesion W_{ad}: $G_c \propto W_{Ad}^n$, where the exponent n is a function of the orientation of the metal constituent. They found that the value of n for the (100) interface plane of niobium is 1.9, and that for the (110) interface plane of niobium is 3.

The leveling off in interface fracture toughness at a silver level of 4.2 monolayers implies that the silver coverage reached 100% at a level of 4.2 monolayers. For the interface without silver, the work of adhesion (W_{ad}) is that of pure niobium/sapphire: 800 mJ/m^2 [6]. For interfaces that have 100% coverage of silver, it was found that the interface fracture occurred at the silver/sapphire interface [7], which has a work of adhesion of 150 mJ/m^2 [8]. Assuming a linear interpolation of the work of adhesion for intermediate value of silver coverage, Fig. 2a can be replotted as a function of the work of adhesion (Fig. 2b). A least square fit of this curve using a power law function gave a value of 3.0 for the exponent n in Eq. 3. This result is in very good agreement with the value of 3.0 obtained by Elssner *et al*. [2].

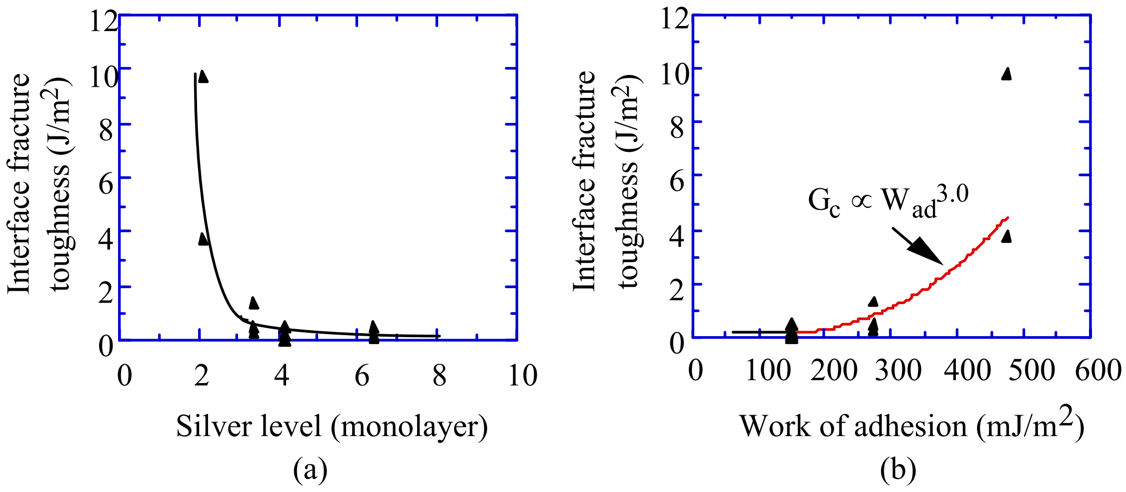


Figure 2: Interface fracture toughness of niobium/sapphire interface as a function of (a) silver level at the interface, and (b) work of adhesion of the interface, and a least squares power law fit yielding n = 3.0.

Microwedge scratch test

Samples with and without silver at the interface experienced interface delamination under the microwedge scratch test. As shown in Fig. 3a, a portion of the film with a constant width was spalled. The tangential load at which the interface delamination occurred was recorded, and the strain energy release rate is calculated by Gerberich et al. [9] A decrease in interface fracture toughness due to the presence of silver at the interface is observed. The average interface fracture toughness for the sample without silver at the interface is 12.44 J/m^2, while the average interface fracture toughness for the sample with silver at interface is 4.54 J/m^2. The estimated values of the interface fracture toughness are consistent in magnitude with that of other metal/ceramic system where for W/SiO_2 interface G_c was found to be 16 J/m^2 and 4 J/m^2 for 1.5 μm and 0.5 μm thick films, respectively [10]. This result is also consistent with the silver effect found by the microscratch test where the presence of silver weakened the interface of niobium/sapphire.

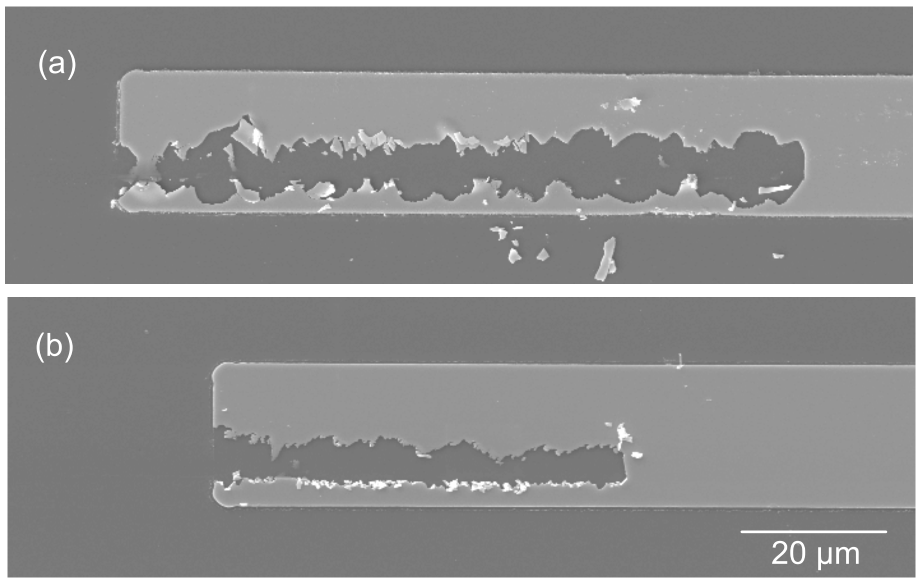


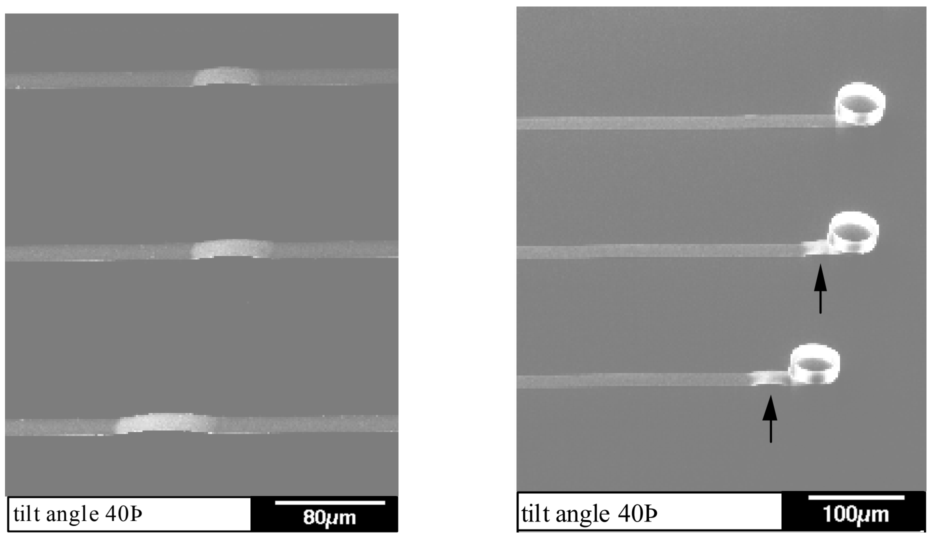
Figure 3: Micrographs of microwedge scratch tracks of (a) the PVD sample with 6.4 monolayer of silver at niobium/sapphire interface , and (b) a PVD sample with no silver at the interface.

Analysis of buckles and curls in patterned lines

Interface fracture toughness was also estimated from the delamination of patterned niobium lines on sapphire substrates. Both curls and buckles were found on some PVD samples. Buckling usually occurs when the film detaches from the substrate in the middle of the line, and curling occurs when the detachment is at one end of the line.

Interface fracture toughness from buckled lines
Buckling was observed for niobium films on sapphire substrate in the patterned line forms, with interfacial silver levels range from 2.5 monolayer to 7.6 monolayer. Figure 4a shows a representative micrograph of the buckles. The buckles indicate that the residual stress in the niobium film must be compressive. The buckle height and length for buckled lines were measured from the photo.

The stress in the niobium film can be determined using the analysis of buckle height given by Hutchinson and Suo [11]. The values of the film stress and the interface fracture toughness for lines that delaminated in the form of buckles ranges from 1.17 GPa to 5.57 GPa in compression, and the interface fracture toughness ranges between 0.62 J/m^2 and 13.6J/m^2. Given a 3% error in the measurement of the buckle height, the error in the film stress and interface fracture toughness is less than 5%.



(a) (b)

Figure 4: SEM pictures of (a) buckled niobium lines on sapphire substrate (PVD, 3.0 monolayers of silver), and (b) curled photoresist/niobium bilayer lines on a sapphire substrate with lines detached from the substrate at the niobium/sapphire interface (PVD, 2.1 monolayers of silver). The arrows point to buckles.

While the magnitude of the stress is not unreasonable for niobium films given hardness measurement of 6 GPa [12], the reason that these films are in compression is unknown. A possible explanation for the formation of the buckles that does not require compressive residual stress in niobium is that the buckles formed at an earlier stage under external force induced by processing or an interface defect (e.g. gas bubble at the interface), causing the niobium to yield. However, optical inspection of the sample showed no observable defects before the photoresist was stripped off.

Interface fracture toughness from curled lines
Figure 4b is a SEM micrograph of the PVD sample with 2.1 monolayers of silver at the niobium/sapphire interface . The photo was taken after the dry etch step when lines were first observed to detach from the substrate. The final step of the photolithography process (stripping the photoresist) was omitted from this sample. Therefore the sample is a bilayer with a 1.35 μm thick photoresist layer on top of a 0.1 μm thick niobium film, deposited on a sapphire substrate which was pre-deposited with silver. As shown in Fig. 4b, the lines were detached from the substrate at one end. The detached portion of the bilayer (photoresist and niobium) curled up, indicating that there was a stress gradient in the bilayer system in which the stress in the photoresist is tensile relative to the niobium film. The observation of buckles next to the curled ends indicates that the stress in the niobium film must be compressive. Given the radius of the curvature, R, of the curls, and the niobium film stress of -1.32 GPa determined from the buckling analysis on a sample with similar deposition condition , the stress in the photoresist is estimated to be 38 MPa in tension.

The fracture toughness of the interface, determined using the analysis in ref. [11], is 0.95 J/m^2. As shown in Fig. 4b, both buckling and curling occurred on the same sample. This can be explained by the stress states in the photoresist and the niobium film. Buckling occurs when the detached segment is bounded by an attached portion of the film, and at least part of the film thickness is in compression. Curling occurs when the detachment extends to the end of the line and there is a stress gradient in the film. In this way, buckling and curling on the same sample and even in the same line is not inconsistent. The photoresist/niobium bilayer buckled once an interface crack was formed, due to the compressive stress in the niobium film. When the buckle formed, the previously tensile photoresist was driven even more tensile. This is the case for the buckles observed next to the curls in these lines. However, once one end of the buckle was detached from the substrate and the constraint from the substrate was removed, the photoresist/niobium bilayer, subjected to the tensile stress in the photoresist and the compressive stress in the niobium, curled in the opposite direction.

No clear trend of the effect of silver on interface adhesion can be established based on the results from delamination of patterned lines. All the PVD samples that had interface delamination in the form of either buckles or curls have silver at the interface, ranging from 2.1 monolayers to 6.5 monolayers. The sample without silver at the interface did not show any interface failure, indicating a stronger interface. However, two other samples that have a relatively high interfacial silver level (4.2 and 7.6 monolayers) did not have any interface failure either.

Effect of IBAD on Interface Fracture Toughness

Ion beam assisted deposition (IBAD) was used to establish the interfacial orientation relationships of either (110) Nb || (0001) sapphire and [001] Nb || $[1\bar{1}00]$ sapphire or (110) Nb || (0001) sapphire and [001] Nb || $[11\bar{2}0]$ sapphire. Silver was introduced at the interface of these samples so that a comparative study could be conducted between the samples with only silver at the interface and samples with both silver and strong in-plane orientation relationship at the interface. The silver level ranged from 0.7 to 6.5 monolayer for the set with the nominal thickness of 100 nm, and 0 to 6 monolayers for the set that had nominal film thickness of 500 nm. This silver level range is similar to that in the study of the effect of silver on interface fracture toughness in PVD samples.

No interface fracture was observed in any of the IBAD samples using the microscratch test. The stress state in the IBAD films was more compressive than that in the PVD films [14], and compressive stress is expected to promote interface delamination in the microscratch test. Therefore, the absence of delamination in the IBAD films indicates a strong interface. All the scratch tracks were similar to that shown in Fig. 1b in which the indenter tip simply ploughed into the niobium layer and eventually broke through the interface to make contact with the sapphire substrate. Even samples with the highest silver level (6.5 monolayers) exhibited strong interfacial adhesion such that there was no observable delamination.

Results of the microwedge scratch test revealed a stronger interface for IBAD samples as compared to the PVD sample as well. Only the sample with the highest amount of silver at the interface (11.4 monolayers) showed delamination. The interface fracture toughness for this sample was 107.91 J/m^2, much higher than that of the PVD samples measured with the same technique (4.54 J/m^2 and 12.44 J/m^2). The IBAD sample without silver at the niobium/sapphire interface showed no interface delamination. The wedge tip ploughed into the niobium film, indicating a strong interface. Delamination of patterned lines on sapphire substrate also indicated a stronger interface for the IBAD samples. Six out of nine PVD samples showed line delamination in the forms of either buckles or curls, while only the one sample with the highest silver level at the interface (6 monolayers) of the four IBAD samples had line detachment from the substrate after the dry etch step. It was found that the delamination occurred at the niobium/sapphire interface. Failure occurred by curling at the end of the lines, similar to that shown in Fig. 4b. The average radius of curvature of the curls was 28 μm. Using the stress of -184.9 MPa obtained from substrate curvature measurement, the interface fracture toughness was found to be 3.22 J/m^2, almost 3.5 times higher than that for the PVD sample with less silver (2.1 monolayer) measured by the same technique (from curls).

Another cause of the strong interface for IBAD samples is ion mixing at the interface. Interface mixing is a common observation in IBAD samples due to ion bombardment during film deposition. Interface mixing is determined via Rutherford backscattering (RBS) analysis. RBS analysis of both PVD and IBAD samples showed that the interface of the IBAD sample was mixed, compared to that for the PVD sample. Mixing at interface usually promotes the adhesion between the film and substrate [13], and is a likely cause of the increased interface fracture toughness exhibited by the IBAD samples.

SUMMARY

Although results of interface fracture toughness measured from different tests, and sometimes within the same test, are not always consistent, general trend of the effect of silver has be established where the interface fracture toughness decreases with the amount of silver at the niobium/sapphire interface. Furthermore, the microscratch test results showed that the interface fracture toughness was related to the work of adhesion through a power law relation with the exponent equals to 3, supporting the result of Elssner *et al*. [2]. The ability to produce interface delamination depends on the test technique, but the values of interface fracture toughness obtained from different techniques fall into the same range (tens of J/m^2 to tenth of J/m^2). Ion bombardment during film deposition (IBAD) significantly increased the interface fracture toughness. Both ion mixing and development of an orientation relationship at the interface enhance the adhesion. The high interface adhesion of the IBAD niobium-sapphire system can be attributed to either one of the two factors or a combination of the two. Ion mixing is believed to be the primary cause.

ACKNOWLEDGMENTS

The authors would like to thank Dr. W. W. Gerberich and Dr. J. Nelson for providing help on microwedge scratch test. Qiong Zhao helped on preparing the samples used in the microwedge scratch test. The authors acknowledge the Michigan Ion Beam Laboratory for Surface Modification and Analysis and the Electron Microbeam Analysis Laboratory at the University of Michigan for the use of their facilities. This work was supported under NSF grant #DMR-9411141.

REFERENCES

1. H. Ji, G. S. Was, J. W. Jones, and N. R. Moody, (1997) *Mat. Res. Soc. Symp. Proc*., Vol. 458, p 191.
2. G. Elssner, D. Korn, and M Rühle, (1994) *Scr. Metall. et Mater.* 31, no. 8, 1037.
3. M. P. Seah, (1980) *Acta Metall*., 28, 955.
4. J. R. Rice, Z. Suo, and J. S. Wang, (1989) In: *Metal-Ceramic Interfaces*, M. Rühle, M. F. Ashby, A. G. Evans, and J. P. Hirth, (Eds), Pergamon Press, Oxford.
5. H. Ji, G. S. Was, J. W. Jones and N.R. Moody, (1997), Proc. Mater. Res. Soc., Materials Research Society, Pittsburgh, vol 458, p. 191.
6. G. Elssner, T. Suga, and M. Turwitt, (1985) *J. Phys. (Orsay*), 46-C4, 597.
7. D. Korn, G. Elssner, H. F. Fischmeister, and M. Rühle, (1992) *Acta. Metall. Mater*. 40, suppl., S355.
8. M.G.Nicholas, (1989) In: *Surfaces and Interfaces of Ceramic Materials*', p. 393, L.-C.Dufour (Ed), Norwell, MA, Kluwer Academic.
9. M. P. dE Boer, M. Kriese, and W. W. Gerberich (1997), *J. Mater. Res*. 12, No. 10, 2673.
10. M. P. dE Boer, H. Huang, and W. W. Gerberich, (1995) *Mat. Res. Soc. Symp. Proc*., Vol. 356, p. 821.
11. J. W. Hutchinson and Z. Suo, (1992) *Advances in Applied Mechanics* 29, 63.
12. H. Ji, G. S. Was, J. W. Jones, and N. R. Moody, (1996) *Mat. Res. Soc. Symp. Proc*. Vol. 434, p. 153.
13. J. E. E. Baglin, (1986) In: *Ion beam modification of insulators*, p. 585, P. Mazzoldi and G. W. Arnold (Eds), Amsterdam, Elsevier.