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# INDENTATION-INDUCED DEBONDING OF DUCTILE FILMS

Alex A. Volinsky, W. Miles Clift*, Neville R. Moody* and William W. Gerberich
University of Minnesota, Dept. of Chemical Engineering and Materials Science, Minneapolis, MN 55455, volinsky@cems.umn.edu
* Sandia National Laboratories, Livermore, CA 94550

## ABSTRACT

Thin film adhesion can be measured by means of the nanoindentation technique [1]. In the case of a ductile film (Cu, Al, Au, etc.) well adhered to a brittle substrate, plastic deformation in the film acts as an energy dissipation mechanism, preventing film debonding. Depositing a brittle layer of W (about 1 micron thick) on top of the film of interest increases the driving force for delamination, thus solving the problem [2]. Indentation produces circular delaminations (blisters), sometimes two orders of magnitude bigger than the indenter contact radius. Thin film adhesion was shown to scale with the film thickness, approaching the true work of adhesion of 0.8 J/m$^2$ for Cu films less than 100 nm thick [3].

Conceptually it is important to know along what interface the fracture occurs during the blister formation. Auger electron spectroscopy (AES) has been used to determine where fracture occurs for different film systems. Cu films on $SiO_2$ failed along the Cu/$SiO_2$ interface. Fracture of Cu films with a 10 nm adhesion-promoting Ti underlayer occurred along the Ti/Cu interface. Significantly, Ti increased the thin Cu film adhesion by a factor of ten. Blisters were removed from the substrate, and the fracture surface was analyzed. In the case of thin Cu films, crack arrest marks were found upon blister removal, and represent the shape of the crack tip [4]. AFM has been used to determine the geometry of the marks. The main component of the arrest marks is carbon, which comes either from the diamond tip or from the hydrocarbons adsorbed on the newly formed surfaces in the indentation process.

## INTRODUCTION

Cu is a new interconnect material for microelectronics applications, and Cu/dielectric adhesion is one of the main reliability issues. It is important to assess a thin film's practical work of adhesion quantitatively. The practical work of adhesion, $W_p$, consists of the thermodynamic, or also called true work of adhesion, $W_T$, and other energy dissipation terms in the film ($U_f$) and substrate ($U_s$):

$$W_P = W_T + U_f + U_s \quad . \qquad (1)$$

Quite often plasticity at the crack tip acts as an energy dissipation mechanism.

In the case of ductile or strongly adhered films, it is often impossible to cause film delamination from the substrate by means of indentation. Ductile thin films cannot store enough strain energy necessary for crack initiation/propagation. Instead of forming blister delaminations, ductile films on a brittle substrate tend to yield, forming plastic pile-up around the indenter. Deposition of a hard layer, capable of storing sufficient amounts of elastic energy over the film of interest, can result in multilayer debonding. In the case of Cu thin films up to 3 μm thick, a one-micron thick W superlayer is enough to produce indentation-induced blister delaminations.

## EXPERIMENT

Cu films of eight thicknesses between 40 nm and 3 μm were sputter deposited on top of oxidized Si wafers with and without a 10 nm thick Ti adhesion-promoting layer. All films were passivated with a 1 μm thick layer of W for adhesion measurements (Figure 1). Thin film deposition and adhesion measurement details are described in [3]. A 1 μm radius conical diamond tip was used in all indentation experiments. In our previous study [3] we looked at the adhesion of Cu thin films with and without a 10 nm Ti adhesion-promoting underlayer as a function of Cu film thickness (Figure 2). On average, for Cu (under 100 nm thick) without a Ti underlayer, 0.8 J/m$^2$ was measured. This value corresponds to the thermodynamic work of adhesion of Cu to $SiO_2$ ($W_T$) measured by the contact angle technique [6]. This means that for films less than 100 nm thick there is almost no plastic deformation at the crack tip [3, 5]. For thicker films there is a definite contribution of crack tip plastic deformation ($U_f$) to the practical work of adhesion ($W_p$), which scales with the film thickness (Figure 2).

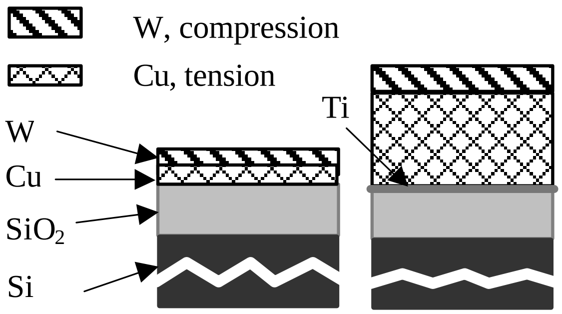



**Figure 1. Thin film system.**

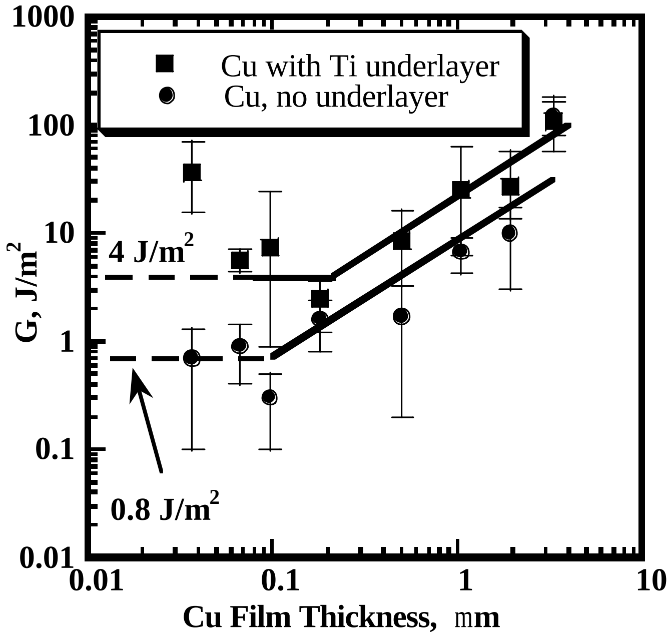



**Figure 2. Cu film adhesion as a function of film thickness.**

For Cu on TiW, the thermodynamic work of adhesion is 2.2 J/m$^2$ [6], which is about half the measured practical work of adhesion of Cu thin films with Ti underlayers. Following [3], the plastic zone size at the crack tip can be calculated if thin film adhesion is known:

$$G = R_P \frac{s_{YS}}{E}\left\{\ln\left(\frac{R_P}{b}\right) - 1\right\} \qquad (2),$$

where $G$ is thin film's practical work of adhesion, $E$ and $s_{YS}$ are it's Young's modulus and yield stress, $b$ is the Burger's vector, and $R_P$ is the plastic zone size at the crack tip. Given the practical work of adhesion of 4 J/m$^2$ and 620 MPa Cu yield stress [9], the plastic zone size at the crack tip is calculated to be 12 nm for Cu film under 100 nm thick with a Ti underlayer. Though the TiW/Cu and the Ti/Cu interfaces are different, it seems that there may be a plastic term contribution even for the thinnest Cu films with a Ti underlayer. Based on the knowledge of film yield stress, several models were proposed to quantify Cu film adhesion as a function of film thickness [3, 5, 7].

## FIDUCIAL MARKS

In our previous study [4] circular crack arrest marks (fiducial marks) were found on the substrate side, and corresponded exactly to the blister original diameter. The marks' geometry was proposed to represent the crack tip opening angle (CTOA). Based on the CTOA measurements the tearing modulus can be calculated using Rice, Drugan and Sham (RDS) analysis [11]. From this the steady state strain energy release rate was calculated for thin Cu films in terms of the thermodynamic work of adhesion [4]. For Cu films under 100 nm thick the true work of adhesion was only a 27% higher than the thermodynamic work of adhesion, which perfectly agreed with the actual experimental measurements (Figure 2).

Conceptually it is important to know along what interface the fracture occurs during the blister formation. To evaluate this blisters were removed with carbon adhesive tape for analysis. Auger electron spectroscopy analysis showed that the failure occurs along the $Cu/SiO_2$ interface [4]. The delaminated area of a 120 nm thick Cu film after blister removal is shown in Figure 3a. As in the previous experiments [4], fiducial marks are clearly seen on the $SiO_2$ side, and correspond to the original blister diameter. Figure 3b shows the removed portion of the film adhered to tape. Note that inside the blister the light areas on the substrate side correspond to the dark areas on the tape side and visa versa.

In our previous study [4] we used Auger electron spectroscopy to identify the contents of the fiducial marks. The results were somewhat inconclusive due to the small volume of the marks' matter and $SiO_2$ charging problems. In the current situation the removed conductive film contains most of the mark (black area inside the blister in Figure 3b), and it is on a conductive tape. This allowed for a more accurate AES analysis. Figure 4a shows an AES line scan data superimposed on the corresponding portion of the SEM image from Figure 3b. The carbon concentration jumps from a background value of 55% to almost 85% inside the mark, at the same time Cu concentration of 30% drops to about 10% inside the mark. Carbon concentration increases in the darker areas, and decreases in the whiter areas of the mark (Figure 4a). Inside the blister the Cu film is covered with a substance that contains carbon. There are three possible sources for carbon: adhesive tape, the diamond indenter [8] and hydrocarbons from the atmosphere [4]. Adhesive tape as a contamination source can be eliminated, since several blisters were removed using a micromanipulator, but the marks were still present.

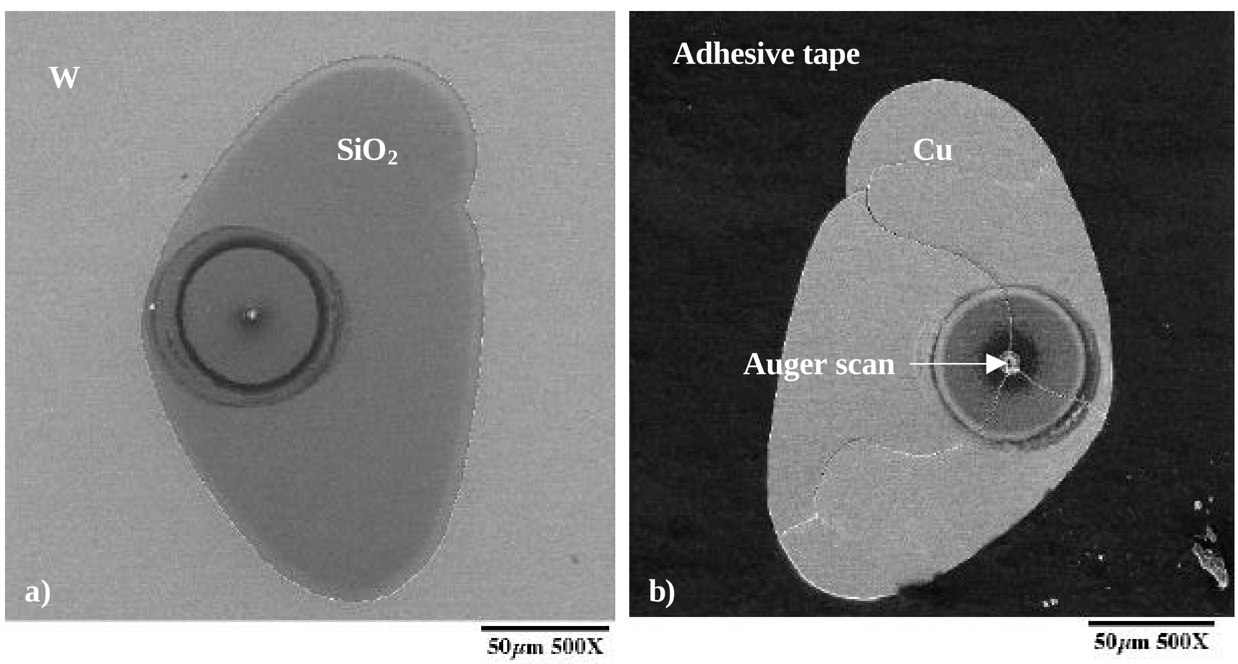



**Figure 3. Cu 120 nm fiducial marks on the substrate a) and on the tape b) sides.**

It is known that diamond indenters wear during indentation of "hard" films. Ti as well as W are known to "suck out" carbon from a diamond indenter [13]. A similar process may occur in our case. Given a 20 nm thick fiducial mark (from AFM measurements) with a 50 μm blister radius, and assuming fully dense carbon ($\rho$=12 g/cm$^3$), one would find $1.9 \cdot 10^{-9}$ grams mass loss per indent. This will result in a significant loss of almost two micrograms for a 1000 indents (a typical number of indents for adhesion testing), assuming that all carbon comes from a diamond tip. On the other hand, W concentration decreases inside the mark, which means that it does not come in the form of a tungsten carbide. One of the ways to find if carbon comes from a diamond tip would be to use a non-diamond tip, and ascertain whether the fiducial marks are still present underneath blister delaminations.

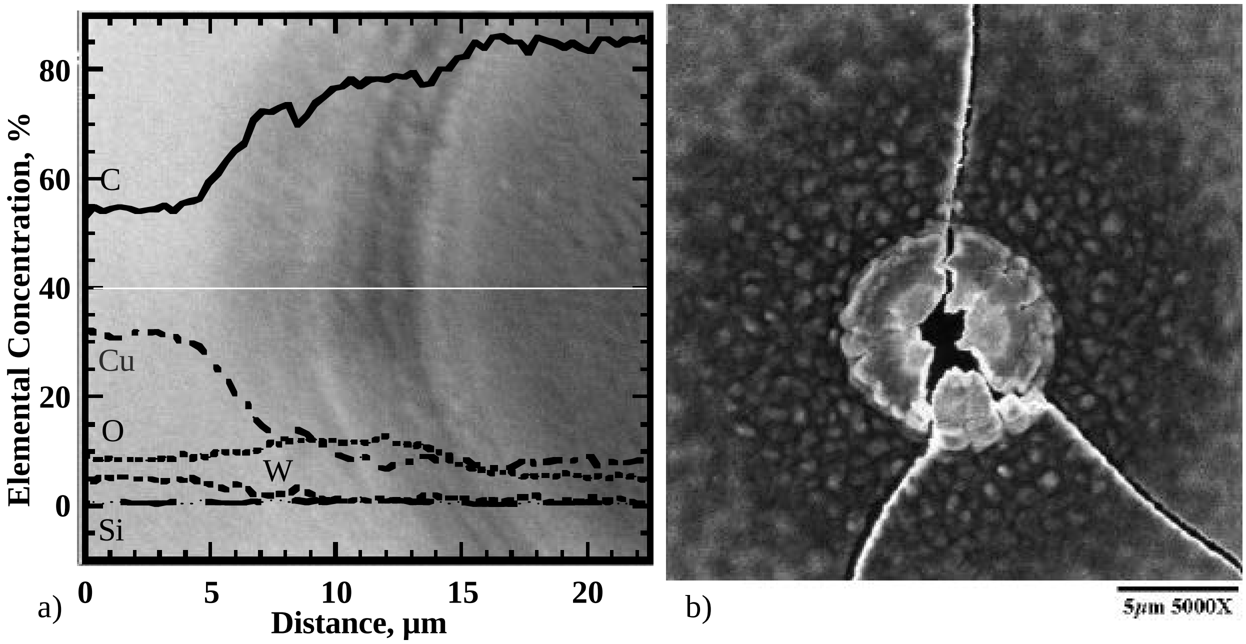



**Figure 4. a) AES scan superimposed on the SEM image from Figure 3 b), b) Center of the blister from Figure 3 b).**

Since the only element besides carbon, which exhibits a concentration increase inside the mark is oxygen (Figure 4a), it is possible that carbon contamination comes from hydrocarbons and moisture in the atmosphere. Due to the radial cracking the two newly formed surfaces are exposed to the atmosphere during indentation-induced delamination. The crack itself can suck relatively mobile moisture and hydrocarbons into its tip, leaving behind the fiducial mark (Figure 3). This is identically analogous to India ink being sucked into a crack tip of bulk $K_{IC}$ specimens [10]. Initially, India ink was put into the crack to outline the stable crack growth region, but this practice was abandoned later due to the finding that this promotes stress corrosion cracking and hydrogen embrittlement. Similarly, it has been shown that the test temperature and hydrogen charging both affect Cu film adhesion [7, 9]. Analogous behavior may then exist in the case of fiducial mark formation, where the interfacial toughness may be easily reduced with the contamination present. Indentation fracture experiments in vacuum or in partial pressure of environmental contaminants should resolve the question of atmospheric influence on the fiducial marks formation and Cu film adhesion. The origin of carbon in fiducial marks will be addressed in greater detail in future work.

The carbon contamination layer on the Cu film (tape) side does not appear to be uniform, since there is structure to it. Figure 4b shows the magnified center region of the fiducial mark from Figure 3b. There is a 10 µm diameter circular residual impression left by the diamond indenter with three radial cracks emanating from its center. The fiducial mark starts right around the indentation contact area within a rough region of carbon-containing black particles (Figure 4b). There is a distinct transition at about 20 µm from the indent center in terms of the surface roughness. This is seen even more clearly on the contact mode AFM images of an 80 nm thick Cu film (Figure 5). The Cu film is relatively smooth outside the original blister delamination area. However, the surface roughness increases inside the blister area, and it increases more closely to the center of the blister. As the transition zone diameter is about twice the indenter contact diameter (Figure 4b), it is possible that the roughness transition is associated with the plastic zone in a thin Cu film. Being capped under the W superlayer, Cu undergoes severe plastic deformation upon indentation. Cu is not allowed to pile-up, being underneath the superlayer, so the plastic zone "tunnels" in the plane of the Cu film [7]. Even though Cu is capped with the superlayer, the effective yield stress of the bilayer composite, $s_{YS}$ can be calculated using the plastic zone size model developed by Harvey et al [12]:

$$s_{YS} = \frac{3P}{2p\,c^2} \qquad (3),$$

where $P$ is the maximum indentation load and $c$ is the plastic zone radius around the indentation. A yield stress of about 1.2 GPa would result for a 250 mN indentation and a 10 µm plastic zone size (Figure 5). This seems to be a reasonable number for a W/Cu bilayer, so the fiducial mark transition zone in fact may correspond to the plastic zone size. Note that these are contact mode AFM images, and a regular sharp SiN contact mode AFM tip does not cause any surface damage.

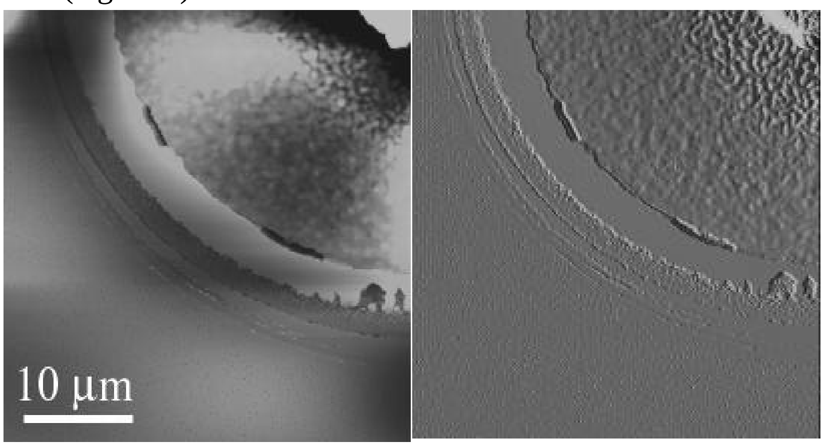
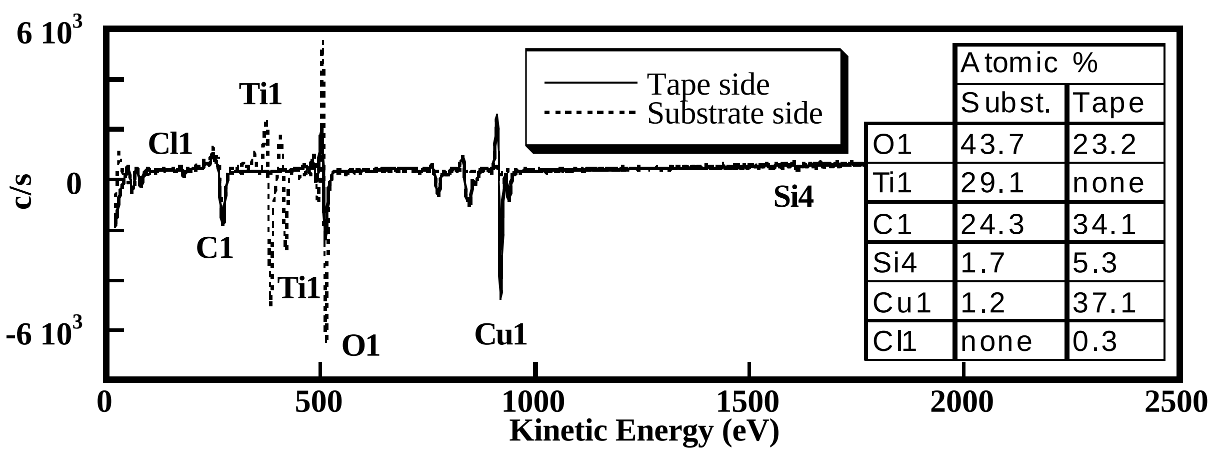



**Figure 5. Contact mode AFM height (300 nm Z range) and deflection images of an 80 nm Cu blister.**

For thicker Cu films having strong adhesion (Figure 2), those over 200 nm thick could not be removed with an adhesive tape (they "survived" the pull-off test). The only Cu film with a Ti underlayer removed was a 40 nm thick film. Unlike films without the Ti underlayer, instead of removing islands of film around the blister (Figure 3), the whole film with the Ti underlayer was removed with an adhesive tape. Some Cu films with the Ti underlayer also exhibited fiducial mark formation. However, no fiducial marks were found for indents, where the indenter did not penetrate through the bilayer thickness, and where no radial cracks were present. It seems like the delaminated interface has to be exposed to the atmosphere for the marks to exist. From Figure 6 showing AES data for the tape and substrate side, it may be concluded that Cu films with a Ti underlayer failed along the Ti/Cu interface. There is no Cu peak on the substrate side scan, but there are two distinct Ti peaks. Opposite, on the tape side there is Cu, but no Ti.




| | Atomic % | |
|---|---|---|
| | Subst. | Tape |
| O1 | 43.7 | 23.2 |
| Ti1 | 29.1 | none |
| C1 | 24.3 | 34.1 |
| Si4 | 1.7 | 5.3 |
| Cu1 | 1.2 | 37.1 |
| Cl1 | none | 0.3 |

**Figure 6. Auger Electron Scans on the substrate and film sides for Si/SiO$_2$/Ti/Cu/W.**

## SUMMARY

Fiducial marks underneath indentation-induced delaminated blisters were characterized by AES in terms of their chemical composition and with Scanning Electron and Atomic Force Microscopy in terms of their microstructure and dimensions. It appears that the carbon contamination (fiducial mark) is present on the inside of the newly formed Cu surface of the blister (Figure 7). Though the exact source of fiducial marks cannot be identified exactly at this point, it will be addressed in future work. Spectroscopy determined that debonding occurred along the Cu/$SiO_2$ interface and with a Ti underlayer, along the Cu/Ti interface. This was accompanied by a nearly order of magnitude toughness increase.

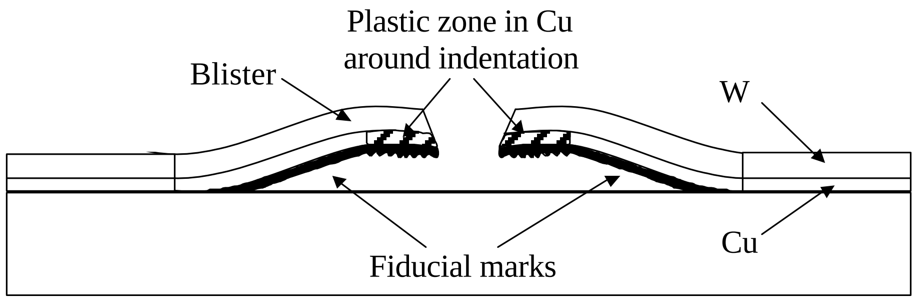



**Figure 7. Fiducial mark schematics.**

## ACKNOWLEDGEMENTS

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