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R.G. Musket
G.R. Wirtenson

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ATOMIC SCALE ENHANCEMENT OF THE ADHESION OF BERYLLIUM FILMS TO CARBON SUBSTRATES

R.G. MUSKET and G.R. WIRTENSON*
Lawrence Livermore National Laboratory, Livermore, CA 94550
*Present address:

ABSTRACT

We have used 200 keV carbon ions to enhance the adhesion of 240-nm thick Be films to polished, vitreous carbon substrates. Adhesion of the as-deposited films was below that necessary to pass the scotch-tape test. Carbon ion fluences less than \(1.6 \times 10^{14} \text{ C/cm}^2\) were sufficient to ensure the passage of the tape test without affecting the optical properties of the films. Adhesion failure of the as-deposited film was attributed to an inner oxide layer between the Be and the carbon. Because this oxide (\(\sim 5 \text{ nm of BeO}\)) was not measurably changed by the irradiation process, these results are consistent with adhesion enhancement occurring on the atomic scale at the interface between the inner oxide and the carbon substrate. This conclusion was supported by Rutherford backscattering (RBS) data, and potential adhesion mechanisms are discussed with consideration of relative contributions from electronic and nuclear stopping.

INTRODUCTION

Many studies have shown that adhesion between various non-reactive films and substrates can be greatly enhanced by the passage of high-energy ions through the interface\(^1\). In general, both the electronic and nuclear components of the ion stopping (i.e., deposition of energy per unit depth or \(dE/dx\)) can provide energy to the interface to promote the enhanced adhesion. However, when the primary energy deposition is dominated by atomic displacements with significant atomic exchange across the interface, the process is called "mixing." In contrast, the term "stitching" has been used to describe such enhancement when the dominant energy deposition mode at an interface is electronic excitation\(^2\).

Although the exact mechanisms responsible for enhanced adhesion via stitching have not been defined, most studies have concluded that bond breaking and reconstruction across the interface is the controlling mechanism\(^2-6\). Determination of exact mechanisms is difficult because the effects are limited to interactions within a few atomic layers of the buried interface\(^1\). We have examined the potential for enhancing the adhesion of Be films to polished, vitreous carbon substrates using ion stitching. We found that these films were only weakly adherent; would sometimes become separated from the substrates upon exposure to moist air (breath fogging), and would not pass the tape test for adhesion. Stitching offered an opportunity to enhance adhesion and yet, preserve the optical properties of the specimen. Stitching does not require many ions/cm\(^2\) and does not result in significant atomic motion at the interface; thus, the surface quality of the films should not be changed by the minimal amount of sputtering, and the smoothness of the interface should not be affected. Considering the ion energy limitation of our 200 kV ion implanter and the 240-nm thick Be films, we were restricted to using light ions (\(Z<7\)) to ensure that the dominant energy deposition process at the Be/C interface was electronic excitation. To minimize potential problems caused by out diffusion of gaseous ions implanted into the substrate or by the presence of chemically dissimilar elements, carbon ions were considered the most promising.

To estimate the \(C^+\) fluences required to stitch the Be films to the carbon substrates, we applied a simple, analytical model\(^7\) that yields the fluence dependence of the fraction of completed interfacial bonds when bond breaking and reconstruction across the interface is the controlling mechanism. The model includes the infraftrack/ultratrack approach for determination of the electronic stopping that is effective for exciting bonding electrons. A range of values for
the one adjustable parameter, \( p \), were considered in the preliminary calculations. This parameter is the probability that an excited bonding electron participates in a bond across the interface. From these preliminary calculations, we concluded that carbon ion stitching using fluences between \( 5 \times 10^{13} \) and \( 1.58 \times 10^{15} \) C/cm\(^2\) should improve the adhesion.

**EXPERIMENTAL CONSIDERATIONS**

The substrate material was Sigriat-K\(^8\), a glass-like carbon made by carbonizing a threedimensional cross-linked resin. This material has a bulk density of 1.55 g/cm\(^3\) no accessible pore volume, a thermal expansion coefficient of 3.5x10\(^{-6}\)/K (20–200°C), and a thermal conductivity of 4.6 W/mK at room temperature. The substrate dimensions were 19-mm dia x 2.9-mm thick. Optical-quality polishing yielded carbon mirror surfaces with surface roughness of \( \pm 5 \) Å rms and bidirectional reflectance distribution functions (BRDF scatter) of \( \pm 1.6 \times 10^{-1} \).

Be films were deposited after the following pre-conditioning steps: 1) the chamber was pumped-down to \( 10^{-5} \) Torr to remove water vapor; 2) at a pressure of 750 mTorr hydrogen, the system was plasma cleaned for 30 min. to remove hydrocarbon contaminants; and, 3) a pre-sputter period using argon, was included to remove any previously built-up oxide from the Be target surface. For our coatings a 5-min. pre-sputter period was used prior to opening the shutter and exposing the substrate. This is half the typical 10-min. process and may have resulted in the deposition of a thin layer of BeO at the substrate/film interface.

The sputtering target (99.3% Be) was a 3-inch dia. cylinder, 1-inch high, with a 0.38-inch wall thickness. The target was the cathode which surrounded a disk-shaped copper anode. A sputter-down arrangement was used with the substrate holder 2.5 inches below the target and supported on an aluminum stage. Be films were deposited at a rate of 7.5nm/sec.

Prior to and after C\(^+\) irradiations, we characterized the coated specimens using RBS and particle-induced x-ray emission (PIXE) with 1.67 MeV He\(^+\) ions. The backscattering angle was 168°, and the x-ray detector was at 90° from the incident beam. The angle between the ion beam and the normal to the specimen surface was 30° with the normal turned from the beam toward the x-ray detector. The beam spot on the specimen was \( 2 \) mm x 2 mm. The program RUMP was used to quantify the RBS data. The resulting thicknesses assume standard densities for elemental layers and a density of 3.01 g/cm\(^3\) for the BeO layers.

Initial C\(^+\) irradiations were designed to determine the fluence, or dose, in C/cm\(^2\) required to provide sufficient adhesion for passage of the tape test. For these irradiations, two specimens were mounted side-by-side on the face of a water-cooled, stainless-steel holder using two screws on the edge of each specimen. The 200 keV C\(^+\) ions with a current of \( \pm 15 \) µA were electronically rastered to irradiate uniformly an area of \( \pm 45 \) cm\(^2\).

For the initial irradiations, we used a movable tantalum shutter in front of the specimen to create four vertical zones, or strips, of constant dose. Thus, the two halves of specimen #4 received \( 5 \times 10^{13} \) and \( 1.58 \times 10^{14} \) C/cm\(^2\), respectively. The doses on specimen #3 were \( 5 \times 10^{14} \) and \( 1.58 \times 10^{15} \) C/cm\(^2\). The highest dose required about 15 min. of irradiation. Specimen #1 served as a control and was not irradiated. After the stitching threshold was determined using specimens #3 and #4, specimen #2 was irradiated uniformly over the entire coated surface to a dose greater than the threshold dose, \( D_\text{th} \).

For the tape test, scotch tape was pressed across the top third of specimens #3 and #4 and over the entire surface of specimen #2. The tape was rubbed to ensure good contact with the coating and then slowly pulled back at about 45° to the surface. The coating was considered stitched if none was removed during the tape test.

**RESULTS AND DISCUSSION**

After the lowest dose of \( 5 \times 10^{13} \) C/cm\(^2\), some of the Be film was pulled off, but most of the Be remained on the carbon substrate. For regions irradiated with doses of \( 1.58 \times 10^{14} \) C/cm\(^2\), \( 5 \times 10^{14} \),
and $1.58 \times 10^{15} \, \text{C/cm}^2$ none of the Be was removed by the tape; however, Be that was shielded by hold-down washers from the irradiating C$^+$ ions was removed by the tape. Thus, the minimum dose required to enhance adhesion sufficiently to pass the tape test is between $5 \times 10^{13}$ and $1.58 \times 10^{14} \, \text{C/cm}^2$, suggesting a $D_{th}$ of $1.1 \times 10^{14} \, \text{C/cm}^2$.

Because (a) the stitching model predicts a saturation of the stitching effect at high fluences; (b) there was no visible change caused by any of the irradiations; and, (c) only about 15 min. were required for the highest fluence, we decided to use the highest fluence on the final test specimen ($#2$). Except for two small regions covered by hold-down washers, the entire surface of specimen $#2$ was irradiated to $1.58 \times 10^{15} \, \text{C/cm}^2$. A tape test of the entire surface removed only the Be from the regions shielded by the washers and the Be that was delaminating prior to stitching. Visually, all specimens were unchanged after the C$^+$ irradiations. No evidence of degradation was observed using magnifications of up to $2000 \times$ on an Aristomet (Leitz) Nomarski phase interference microscope. For specimen $#2$ the combined effects of the Be coating and the irradiation to $1.58 \times 10^{15} \, \text{C/cm}^2$ increased the surface roughness from 5.5 to 8.2 A rms and the BRDF from $1.6 \times 10^{-4}$ to $4 \times 10^{-4}$.

RBS and PIXE were used to characterize the as-deposited films of specimens $#1$, $#3$, and $#4$. After C$^+$ irradiations, we obtained spectra from the low-dose and high-dose regions of both specimens $#3$ and $#4$. For all specimens, the as-deposited analysis was performed at a spot near the center of the specimen. After C$^+$ irradiations, the analyses of specimens $#3$ and $#4$ were obtained near the center of each of the two different irradiation regions.

Figure 1 compares part of the RBS spectrum from near the center of the as-deposited specimen $#3$ with that from the half of specimen $#3$ that received a dose of $1.58 \times 10^{15} \, \text{C/cm}^2$. These spectra show all the features seen for the other specimens. The subscripts "s" and "i" denote the energy corresponding to backscattering from the indicated element at the surface and at the interface between the carbon substrate and coating, respectively. A thin carbonaceous layer ~0.5 nm carbon can be seen at the surface of the specimens. The oxygen peaks at the surface and at the interface presumably result from the presence of thin BeO layers at these two locations (e.g., 2.0 and 5.3 nm thick, respectively, for the as-deposited case). Thus, stitching was required to enhance adhesion between the interfacial BeO layer and the carbon substrate, not between Be and carbon, as originally believed. Between the two oxygen peaks is the oxygen level (1.0 at.%) in the metallic Be layer.

![Fig. 1: Plots of parts of the RBS spectra from the center of specimen #3 in the as-deposited condition and from the half of specimen #3 that received a dose of $1.58 \times 10^{15} \, \text{C/cm}^2$.](image)
The surface oxide thickness is typical of a native oxide on Be; however, source(s) of the oxygen in the metallic Be layer and in the interfacial oxide is not clear. The interfacial oxide may have resulted from sputtering of BeO from the surface of an incompletely pre-sputter-cleaned Be target or from reaction of interstitial water in the surface region of the carbon substrate with deposited Be. Oxygen content of the metallic region of the Be may represent effects of atmospheric oxidation of grain boundaries in the Be or effects of residual contamination during the deposition process. Small differences in the thicknesses of surface oxides (2.0-2.4 nm of BeO) and interfacial oxides (4.3-5.9 nm of BeO) and in the thicknesses of the metallic Be layers (198-2235 nm) can be attributed to variations across the specimen.

Copper (0.09 at.%) can be seen uniformly distributed in depth within the first 225 nm of the metallic Be layer. The aluminum impurity peak corresponds to a thin layer of aluminum (1.7×10¹⁵ Al/cm²) located within the metallic Be layer near the interfacial oxide or, equivalently, to 0.9 at.% Al in a 15 nm layer of Be. Identities of both copper and aluminum impurities were verified by the presence of characteristic x-rays in PIXE spectra from specimen #3.

For specimen #3, the RBS oxygen peaks at the interface between the Be coating and carbon substrate are compared in Fig. 2 for three different doses: 0, 5×10¹⁴, and 1.58×10¹⁵ C/cm². The given overlay was obtained by normalizing peak integrals (to correct for different oxide thicknesses) and aligning peak centroids (to compensate for different thicknesses of Be) to those of the unirradiated case. The shapes of the three peaks are identical within the statistics of the data. A broadening of the peaks from the measured width of 5.3 nm of BeO to 10 nm of BeO would have yielded the simulated curve shown in Fig. 2. Because the width of the spectral peaks were all significantly less than that for 10 nm of BeO, we concluded that the width of the oxygen distribution was increased by < 5 nm of BeO by the highest dose irradiation and enhanced adhesion resulted from effects occurring on the atomic scale (i.e., < 25 inter-atomic distances).

For 200 keV C⁺ ions incident on a layered structure consisting of a 240 nm Be/5 nm BeO/C, TRIM calculations showed that the electronic stopping of C⁺ ions at the interface between the BeO and carbon was 50 eV/Å in BeO and 43 eV/Å in carbon. In these calculations, the densities
were 3.01 and 2.26 g/cm³ for BeO and carbon, respectively. For the infratrack/ultratrack approach, the band gap for BeO (i.e., 10.5 eV) and calculated bulk plasmon for carbon (i.e., 28.9 eV) were used for the characteristic electron energies, and the band gap for BeO and the work function of carbon were used as the energies required to excite bonding electrons. From this calculation, the electronic stopping effective in exciting bonding electrons was found to be 43 eV/Å in BeO and 32 eV/Å in carbon.

Although the relationship between the number of interfacial bonds, b, existing at the threshold dose, Dth, and number of interfacial bonds at steady state, bss, (i.e., for very large doses) is not known from our measurements, a reasonable expectation is that the value of b/bss is significantly less than one at Dth. For the purpose of comparison with our tape threshold dose, the calculated threshold dose will be taken as that corresponding to b/bss = 1/4. With this ratio fixed and Dth = 1.1x10¹⁴ C/cm², the parameter, p, (i.e., probability that an excited bonding electron eventually participates in a bond across the interface) was calculated to be 0.15.

![Fig. 3: Calculated carbon-ion fluence dependence of stitching for a BeO layer on carbon.](image)

Using p = 0.15, the fluence dependence of the stitching model was calculated and is shown in Fig. 3. This curve shows that more than 80% of stitching occurs within a decade of fluence (high x10¹⁴ to high x10¹⁵ C/cm²) and that at steady state almost 30% of interfacial bonds are participating in bonds across the interface. At the highest fluence used in our study, 1.58x10¹⁵ C/cm², the model predicts that maximum stitching has been achieved.

Effects of atomic displacements at the BeO/C interface must also be considered for C⁺ ions passing through the interface with an energy ~90 keV. Creation of atomic vacancies at the interface means that bonding arrangements must be disturbed and bonding across the interface may be induced. TRIM calculations at the interface indicated that an average of ~0.09 vacancies would be created per ion per Å. Considering an approximately 3 Å-thick atom layer on each side of the interface, each ion would create ~0.54 vacancies that could lead to bonding across the interface.

Thus, at the threshold dose of 1x10¹⁴ C/cm², about 5.4x10¹³ vacancies/cm² would have been created. If all of these displacements led to bonding across the interface, then ~ ~ 1.35x10¹⁴ interfacial bonds per cm² would have been created, assuming an average of ~2.5 bonds per atom. This would account for ~3% of the average number of interfacial bonds, even if all
vacancies led to interfacial bonds, the stitching model predicts that electronic excitation accounts for at least 70% of the adhesion enhancement at the threshold dose.

CONCLUDING REMARKS

We have shown that adhesion of 240 nm thick Be films to polished, vitreous carbon substrates can be dramatically enhanced by stitching with 200 keV carbon ions. Although the adhesion of the as-deposited films was below that necessary to pass the scotch-tape test, C⁺ doses greater than ~1x10¹⁴ C/cm² were sufficient to enhance the adhesion enough to ensure passage of the tape test without significantly affecting the optical properties of the films.

Using the experimental threshold dose Dth of 1x10¹⁴ C/cm², we extracted a value of p = 0.15 for the single parameter of the stitching model. With this value of p, the model predicts that for doses exceeding about 1.5x10¹⁵ C/cm², maximum stitching would be achieved. Thus, at the highest fluence used in our study, 1.58x10¹⁵ C/cm², the model predicts that maximum stitching was achieved with almost 30% of interfacial bonds participating in bonds across the interface.

An improved understanding of the mechanisms is needed to optimize the irradiation. For example, by changing the ion energy at the interface, we can change the relative amounts of electronic excitation and vacancy production and correlate these changes with differences in the observed threshold dose for stitching. In addition, we need to make quantitative measurements of adhesion changes caused by the ions, to understand interfacial bonding strengths and to allow proper comparison with the stitching model.

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REFERENCES

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