Thin film bonding using ion beam techniques—A review

by J. E. E. Baglin

Ion beam technologies provide a variety of well-proven means for creating or enhancing strong, stable, direct adhesion of thin films deposited on substrates. Interface chemical bonding and structure are critical. Yet success with such approaches has been reported for a great variety of systems that have little or no bulk chemical affinity, including metals, polymers, ceramics, and semiconductors. This review paper describes the established techniques of reactive and nonreactive ion beam sputtering, ion-beam-assisted deposition, ion implantation, and ion beam stitching. It then presents representative examples of adhesion enhancement selected from the current literature, in order to clarify the roles of interface chemistry, morphology, contaminants, and stability. The review offers a basis upon which interface tailoring for adhesion may be planned in order to optimize both performance and fabrication of specific materials systems.

Introduction

The formation of a well-attached thin film coating on a substrate of choice is increasingly becoming a critical manufacturing process, in a wide range of industries and applications. Thin coatings for protection of metals against corrosion are ubiquitous; hard or tough diamond-like films are required for protection against wear; metal coatings on polymers or ceramics provide optical reflection and electrical conductivity; microelectronic devices and their packaging systems demand multiple thin film coatings that must all be directly bonded and display good integrity against corrosion and delamination during the multiple steps of wet and dry processing, in addition to stability during the product lifetime. As engineering technologies develop towards the very small (nanostructures) or towards extreme service conditions (aerospace materials), it becomes increasingly important to be able to bond arbitrary, dissimilar materials directly to each other in a highly durable way.

In earlier days, bonding of many systems could only be accomplished with an active intermediate layer of adhesion-promoting material. Today, the use of a macroscopic added layer can be unwelcome for many reasons, e.g., the layer may have its own serious limitations of integrity and durability. In the semiconductor and data recording technologies, additional layers add thickness and complexity to the device structure, they require additional manufacturing steps (and cost), and each added layer/step represents an added exposure to faults in the processing.

In recent years, it has become evident that many such joining processes can be accomplished best (and with high performance) by custom-tailoring the interface at the nanoscopic/atomic scale [1–5]. The approach is to intentionally control interface contamination, interface morphology, and interface chemistry, in order to maximize the quality of the direct attachment of the film to the desired substrate. Strong and stable bonding has been achieved easily for such unlikely systems as vapor-deposited copper or gold on ceramic surfaces, or on polymers such as Teflon®.

The tools whereby this direct bonding is accomplished have evolved in parallel with our understanding of thin film adhesion mechanisms. Today we have ready access to a variety of ion beam tools capable of selective interface tailoring, whose diversity enables us to select the most effective and economical approach for a given bonding requirement, and to choose manufacturing tools that are generally compatible with standard thin-film coating systems. As we shall see, the low-energy, broad-beam Kaufman ion source provides the greatest proven versatility and capability for *in situ* tailoring of thin film interfaces when the coating is deposited in vacuum [2]. In some cases, especially where irregular surfaces are involved, plasma immersion techniques may be preferred. For thicker films or pre-deposited coatings, higher-energy ion irradiation may be the most effective approach.

In this paper, we review first the intrinsic issues of creating a good-quality bonded interface, and outline the mechanisms whereby the various ion beam technologies can address these issues. We then proceed to quote a representative variety of examples of published research, to illustrate the breadth of possible applications and also to indicate the basic underlying mechanisms whereby adhesion has been achieved or enhanced in each case.

Adhesion performance

The measures of "good" adhesion performance are usually specific to the application in question. Testing criteria address the particular function required, e.g., resistance to delamination, corrosion, peeling, shear, wear, or thermal stress [2]. As a practical matter, it is also important for product reliability that the bonded interface be in a thermodynamically stable state (within the service temperature range), so that the adhesion will not deteriorate with time.

For thin films, the stability criterion may constitute a problem for reactive couples, such as nickel on silicon, where substantial interdiffusion to form a silicide layer can occur at only 225°C. In this case, the silicide does serve to bond the metal to the substrate. However, we can not always presume that such a grown layer bonds well to both parent layers. In principle, the stability criterion is best served if any such intermediate reactions have gone to completion (e.g., all the Ni has been consumed to form silicide). For film/substrate couples that have no bulk chemical affinity, however (e.g., metals on ceramics), it would appear that the interface is stable precisely because no chemical bonding will occur! Clearly then, a "stable" bonded interface must in general involve some intermediate joining layer (whose thickness can be as little as a monoatomic layer). That layer will be chemically stable, and will be intrinsically linked to the materials of both film and substrate. This joining layer may perhaps be made up of chemical complexes involving the constituents of both film and substrate, stabilized by being confined in a two-dimensional configuration, but not necessarily corresponding to bulk phases. Alternatively, such a layer complex might require the presence of an additional reactive chemical species in order to join the film and substrate; however, in keeping with the stability criterion, the supply of such a reactant should be limited (and may be simply an interface monolayer or less).

The function of such an altered interface layer is simply to lower the interface free energy γ_{int} in order to maximize the energy of adhesion

$$W_{ad} = \gamma_{film} + \gamma_{subs} - \gamma_{int},$$

where γ_{film} and γ_{subs} are surface free energies.

Whether or not such a chemically stable joining entity exists will depend on the system in question. In some cases, the addition of a reactant species will work (e.g., the common technique of bonding metals on glass via a thin layer of Cr/Cr oxide). In some cases, an interface complex can be formed after alteration of the surface composition of a compound substrate (e.g., reduction of oxygen in the Al_2O_3 surface enables formation of a stable Cu–O–Al interface complex when a Cu film is added [6]. In some cases, it is sufficient simply to introduce disorder at a normally terminated substrate surface in order to induce new chemical bond configurations with an added layer (e.g., breaking up a polymer surface in order to generate functional groups at the interface through scission).

Ion beam strategies

Ion beam techniques provide a well-controlled means of creating the low-energy chemically stable joining layers described above. In addition, they can be used to enhance adhesion in other ways, as shown schematically in **Figure 1**. Comprehensive reviews of these techniques may be found in references [1–4].

Low-energy sputtering in situ

When a thin film is to be vacuum-deposited, an *in situ* pre-sputtering treatment of the substrate can generally improve subsequent adhesion. Large-area ion sources are available for the purpose, with their ion energy range variable between 100 eV and a few keV. An inert species such as

Ar will clean the substrate surface of most contaminants, which is generally a very desirable procedure. The process will also break up surface bond chains of a polymer substrate or the terminating layer of a metal oxide, possibly exposing active sites on which a promptly added metal film may bond covalently.

On some inhomogeneous substrates, the ion bombardment will produce a roughened surface (e.g., $Ar^+ \rightarrow$ molded Teflon), which can strengthen the interface formed by virtue of its fracture toughness, as well as its increased net contact area.

At energies less than 500 eV, Ar^+ bombardment of a compound substrate can also exhibit preferential sputtering [7], leaving a surface whose elemental composition is determined by the ion collision kinetics and surface binding energies. The process affords some latitude for tailoring a surface composition as a precursor to forming a stable interface complex when a film is subsequently deposited.

A further option is the admixture of a reactive species such as oxygen during the pre-sputtering process. This can serve to enhance the removal of surface carbon impurities, and also possibly to modify the substrate surface chemistry.

• *Ion-beam-assisted deposition (IBAD)*

The low-energy Kaufman ion source may also be used to bombard the receiving surface throughout the deposition of the film. In addition to the interface benefits of pre-sputtering, this process produces films that are denser and freer from intrinsic stress than they would otherwise be. Much of this results from the increased kinetic activity at the receiving surface, leading to closer equilibrium packing of the arriving atoms. This reduction of film stress, in turn, lowers stored stress energy that would otherwise assist interfacial failure.

• *Reactive ion implantation*

A controlled quantity of a reactive ion species may be added in the vicinity of an already formed film/substrate interface by means of ion implantation. The ion energy required will depend on the film thickness and the ion species. (Tabulation of ion ranges may be found in reference [8]; complete ion distributions may be calculated using the TRIM software [9].) This process would often require the use of an implantation accelerator, and it therefore lacks the simplicity of low-energy processing. It does, however, bring some special bonuses. Because of the inevitable range straggling of the ions, the interface region will be modified in a graded way. The implanted ions will also introduce some ballistic mixing in the interface region. This can result in a graded interface "layer" showing high fracture toughness and excellent integrity.

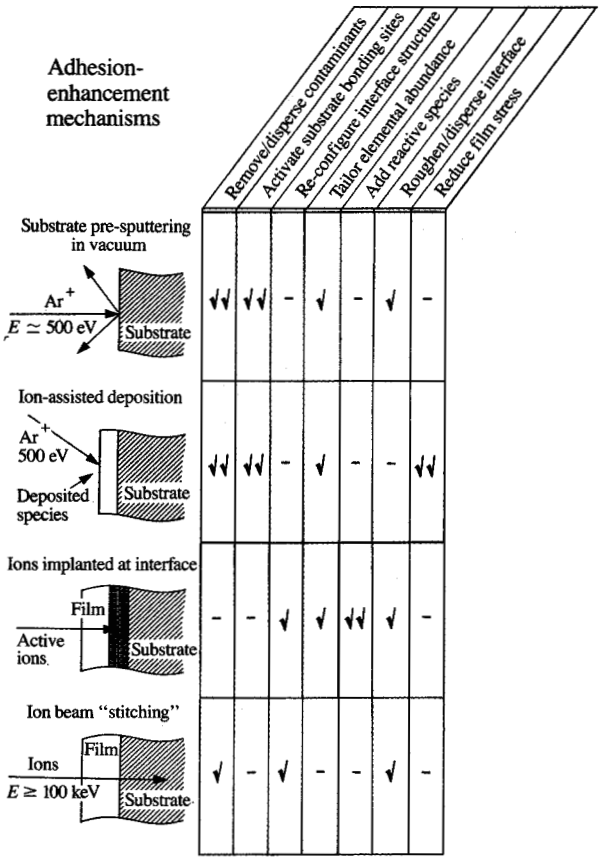

Figure 1

Mechanisms for ion beam enhancement of thin film adhesion.

• *Ion beam stitching*

In this technique [10, 11], energetic, inert ions pass through an existing film and its interface, and continue deeper into the substrate. Each ion creates a sheath-like "collision cascade" within the solid, densely populated by secondary electrons from ionizing collisions and some nuclei recoiling from ballistic nuclear collisions. The effective radius of this region is usually a few nanometers, and it can experience an extremely high instantaneous rate of energy deposition (of order 1 eV per atom). Models indicate that the atoms within each such cascade attain a near-Boltzmann distribution of energy after $\sim 10^{-11}$ s, corresponding to a "temperature" of several thousand degrees K. This energy disperses into the surrounding solid within $\sim 10^{-9}$ s. During this brief period of high atomic mobility, substantial rearrangement of atoms within

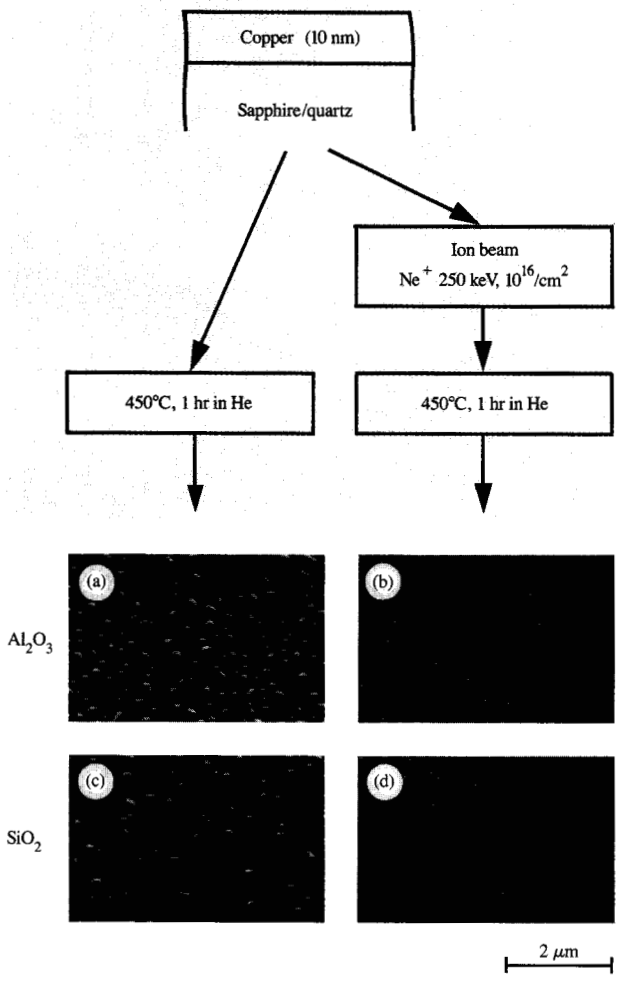

Figure 2

Stabilization of a thin (10 nm) layer of Cu on sapphire, (a), (b), and silica (c), (d). Ion stitching produced a "wetted" surface showing no tendency to form balls/islands upon heating. (From reference [18], reproduced with permission.)

the cascade can occur [12]. In reactive bilayer systems, where a thermodynamic driving force would exist for interdiffusion to form compounds (e.g., silicides), substantial layer diffusion ("ion beam mixing") is indeed found to occur. Conversely, at interfaces of immiscible materials (e.g., Cu–W), intermixing is thermodynamically not favored, and only slight ballistic mixing is found. Evidently the cascade causes momentary bond dissolution and atomic mobility, from which the system reconstructs in the direction expected from normal thermodynamics.

We now invoke the hypothesis that in some systems of bulk-incompatible materials, stable interface complexes may exist, if only the constituent atoms are brought into proximity. It is postulated that such complex clusters may form randomly within the collision cascade, producing local bonding across the interface. However, since each succeeding ion will disrupt any such clusters that it encounters, the effectiveness of this mechanism will be somewhat limited.

Experimentally, ion stitching has provided significant adhesion enhancement for an enormous variety of systems—perhaps because of the very randomness of its action. (See references [3] and [5].) Recent examples, in which Cu and Al are bonded on SiO_2, are presented in references [13] and [14].

A further apparent benefit of ion stitching is its ability to overcome or disperse contaminant layers.

Irradiation of most polymer films or substrates with high-energy ions leads rapidly to structural degradation of the polymer from cross-linking and/or chain scission. This imposes severe practical limits on the acceptable dose of ions used for stitching a polymer; however, the technique can still produce major adhesion enhancements within such dose limitations.

Examples

In the following section, we review briefly some representative published examples of the application of the ion beam techniques discussed above.

- *Stress removal by IBAD*

This approach to enhanced adhesion was used by Barth et al. [15] for the deposition of Cr(1 μm) on steel, concurrently with 6 keV Ar^+ bombardment. In the absence of the ion beam, the presence of high stress led to cracking and weak adhesion of the thick chromium film. By IBAD, with an Ar^+-to-Cr arrival ratio of 0.04, they produced Cr films with negligible stress, correlated with a fivefold increase in adhesion performance (scratch test).

- *Contaminant layers*

Cailler et al. [16] recently reported the successful adhesion of Cu(200 nm) deposited on carbon steel that had been mechanically polished. A thin oxide layer on the polished steel originally led to very low adhesion of the Cu film. After fully removing the oxide by 600 eV Ar^+ etch, they found an increase of a factor of 20 in the film adhesion, according to a scratch test. A similar result was found for Ni deposition on a Ni substrate bearing a native oxide.

The ability of ion stitching to overcome the effect of such a native oxide on Cr was demonstrated by Bøttiger et al. [17]. They found negligible adhesion (peel test <0.1 g/mm) for a film of Cu(70 nm) deposited on air-exposed Cr; after stitching the same sample with 5×10^{15}/cm^2 of 250 keV Ne^+ ions, the film displayed a peel strength of more than 160 g/mm. (A very strong

bond; for comparison, the Scotch Tape™ strength is typically 5 or 6 g/mm.)

• *Interface chemistry and structure: Cu/Al_2O_3 and Fe/Al_2O_3*

Two systems that have received considerable study are $Cu–Al_2O_3$ and $Fe–Al_2O_3$. In view of their chemical similarity, we shall discuss them together.

Interface wetting

Baglin and Clark [18] reported on a novel application of ion stitching. A very thin (≤10 nm) layer of Cu deposited on clean sapphire or silica and then heated at 450°C would normally form quickly into beads or islands, since Cu can not chemically disrupt the sapphire or silica surface to "wet" it. However, ion stitching with 10^{16} Ne^+/cm^2(200 keV) before heat treatment prevented the film breakup (evidently lowering the interface energy) as shown in **Figure 2**. This incidentally demonstrates a practical means of stabilizing very thin coatings on a non-wetting substrate.

Ion beam stitching

"Stitching" with 250 keV Ne^+ ions has been found [6] to raise the adhesion (peel strength) of Cu(70 nm) on sapphire from near zero to ~9 g/mm, as shown in **Figure 3**. The major increase in adhesion for doses of around $6 \times 10^{15}/cm^2$, followed by a plateau for higher doses, is consistent with the model of interface relaxation presented above, in which overlapping cascade areas ultimately benefit the entire interface area, after which repeated cascade disordering can make no further improvement. After heating at 450°C, the adhesion improved to 18 g/mm, implying that the modified interface was thermally stable. Subsequent analysis showed that the bonding layer was no greater than one monolayer deep, which is also consistent with the formation of a thin complex bonding layer.

Ogale et al. [19] and Perez et al. [20] both used Conversion Electron Mössbauer Spectrometry (CEMS) to identify the interface chemical changes occurring when ion stitching was applied to $Fe–Al_2O_3$. Successful adhesion was accompanied by dramatic changes in the CEMS spectrum from interface Fe, as shown in **Figure 4**. In CEMS, photons emitted from a radioactive ^{57}Co source undergo resonant absorption in a test specimen of ^{57}Fe, which then de-excites with emission of conversion electrons, which can be counted. By placing the ^{57}Co source on an oscillating table, the effective energy of the exciting photons may be Doppler shifted, in order to scan the absorption spectrum for ^{57}Fe. Due to hyperfine interactions, the ^{57}Fe absorption profile will be affected by the surrounding electron configuration, and hence the spectrum of hyperfine structure provides information about the chemical bonding state of the ^{57}Fe.

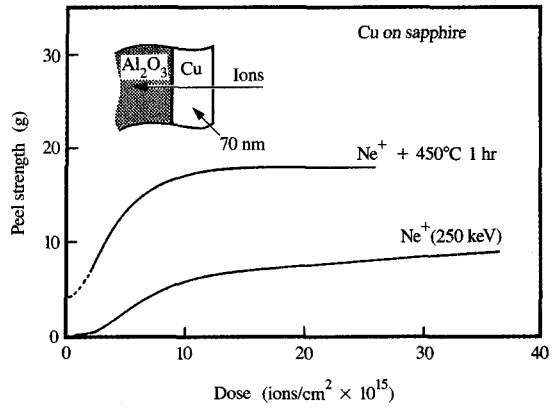

Figure 3

Ion beam stitching of Cu(70 nm) on sapphire. (From reference [3], reproduced with permission.) Thermal stability is indicated by improvement of adhesion after 450°C heat treatment.

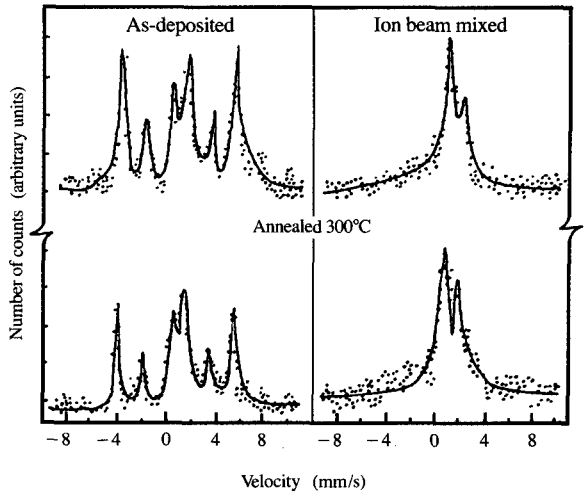

Figure 4

Ion beam stitching of Fe on Al_2O_3. CEMS spectra display the complete conversion of a 2-nm ^{57}Fe interface layer to Fe^{2+} (believed to bond in a ternary oxide like $FeAl_2O_4$), plus some Fe^{3+} oxide. (From reference [19], reproduced with permission.) The stitching process (100 keV Kr^+) was shown to improve adhesion dramatically in a similar study by Perez et al. [20].

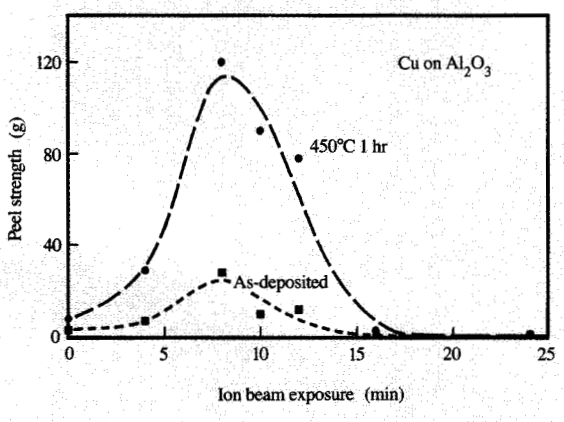

Figure 5

Adhesion enhancement for Cu/sapphire resulting from pre-sputtering the substrate *in situ* with 500 eV Ar ions (50 μA/cm^2) immediately before Cu deposition. (From reference [6], reproduced with permission.)

In these experiments, the interface region was specifically tested by making a special interface layer (2 nm) of ^{57}Fe. The sextet of peaks shown for the as-deposited samples (Figure 4) displays the magnetic hyperfine interaction for Fe in the metallic state (not chemically bonded with the substrate). The profound change to the simple spectrum on the right side of Figure 4 represents conversion of the whole 2-nm ^{57}Fe layer to a mixture of Fe^{2+} and Fe^{3+} bonding. At very large doses of heavy ions, Perez et al. could identify extended ion beam mixing (verified by TEM), in which metallic Al was precipitated while Fe^{3+}(oxide) was formed; however, in both experiments the low-dose effect that was specifically linked to adhesion enhancement was the formation of Fe^{2+}, supposedly bound as a ternary oxide complex similar to $FeAl_2O_4$, and confined to the immediate interface layer.

Pre-sputtering in situ

The power of pre-sputtering a compound substrate was demonstrated by Baglin et al. [6] for Cu–Al_2O_3. Sapphire substrates were bombarded with 500 eV Ar^+ ions using a Kaufman source *in situ*, after which Cu was e-beam deposited immediately. The samples were then annealed at 450°C for 1 hr. The adhesion was reported as 120 g/mm (see **Figure 5**), six times stronger than that obtained by ion stitching. The existence of a preferred interface composition may be inferred from the strong dose dependence of the adhesion; sputtering of the sapphire surface presumably progressively removes minor contaminant layers, and then depletes the oxygen atom layer that would normally constitute the sapphire surface. It is postulated that at some point in this process, both Al and O surface bonds become available for creation of mixed oxide complexes on arrival of the Cu. This model was supported by a parallel *in situ* XPS study which identified a new Cu Auger (LMM) line corresponding to a Cu–O–Al ternary structure. Preferential sputtering is predicted for Ar^+(300 eV) on Al_2O_3, where the surface would be enriched in Al. This effect was recently verified experimentally by Mukhopadhyay and Chen [21], using Ni adsorbates to monitor the oxygen activity at the sputtered Al_2O_3 surface. Our adhesion model is supported by the observation that a similar procedure using Ar^+ pre-sputtering at 8 keV (where less preferential effect is expected) showed poorer population of the ternary peak.

Interface roughness

Although ion beam treatment has not been shown to produce any physical roughening on alumina or sapphire surfaces, the question has often been asked: "How much of the adhesion enhancement may be a consequence of some microscopic surface roughening by the ion beam?". A direct test of this was provided by Chang [22], who prepared Al_2O_3 over pre-roughened substrate surfaces, creating a graded series of roughened "Al_2O_3" substrates. Cu films were then deposited directly (without ion assist), and tested for adhesion. The substrate with 50-nm-wide features of high aspect ratio provided an elevated peel strength of 1.6 g/mm. While this does not compare with the bonding obtained by ion bombardment treatments, it was still about 10× stronger than the adhesion on the smooth substrate. It is reasonable to assume that this effect was entirely geometrical, and that substrate roughening should produce an extremely effective bond if coupled with ion beam treatment that activates the interface chemistry.

Reactive ion beam implantation

Madakson and Baglin [23] implanted Ti^+ (120 keV, 10^{16}/cm^2) at the Cu–sapphire interface and found adhesion to exceed 200 g/mm (clearly greater than that obtained by other passive methods). The success was attributed partly to the formation of metal oxide complexes, and partly to the fracture toughening of the interface region due to nanoscale precipitates of Al_2TiO_5.

In a more recent study, Pawel and McHargue [24] implanted the Fe(100 nm)–Al_2O_3 interface with Cr(300 keV), Fe(300 keV), or Ni(340 keV) at doses of 10^{15}/cm^2, in order to compare the generic ion-stitching benefits with those that may be ion-specific. They found that Cr^+ clearly improved adhesion; Fe^+ also improved adhesion, but to a lesser extent; and Ni^+ had negligible effect. The authors conclude that the Fe^+ effect (purely interface mixing/stitching) is enhanced by Cr^+ as it lowers the

interface free energy, but that it is countered by Ni^+, which must therefore be raising the interface energy. This result appears to highlight the important point that the existence of beneficial interface complexes can not be presumed for all systems; each elemental system must be explored individually in terms of its own chemistry.

An interesting variant on this process was recently published by Pivin et al. [25], who found that pre-implantation of carbon in the surface of Si or metal alloy substrates enabled good bonding of diamond-like carbon films prepared on these surfaces.

- *Interface chemistry and structure: Ni on glassy carbon and Mylar®*

Ion stitching/implantation

In an interesting series of experiments, Galuska [26] compared the adhesion and structure produced by a) ion stitching a Ni film deposited on glassy carbon, using 10^{16} Kr^+/cm^2 to penetrate through the interface, b) reactive implantation of 10^{17} Si^+/cm^2 at the interface, and c) ion beam mixing of Ni/Si/(glassy carbon) using Kr^+ ions. He subsequently examined each interface by XPS. The results are summarized schematically in **Figure 6**. Introduction of the reactive species, whether by implantation or ion-mixing, led to the formation of Ni–Si–O–C complexes that strongly bound the interface. The ion stitching strategy failed as the Kr^+ ions produced a stoichiometric mixed layer of Ni_3C which itself bonded poorly to carbon.

Similar experiments by Galuska [27] for Ni on Mylar also produced adhesion by implantation of Si ions; however, ion mixing of Ni/Si/Mylar produced a layer of SiO_2 at the Mylar surface, to which the Ni layer did not adhere.

- *Interface chemistry and structure: Cu/Teflon; Fe/Teflon*

These systems have also received considerable attention, and again, recognizing their similarity, we shall discuss them together. In both cases, in the absence of ion beam treatment, adhesion of the deposited metal film is negligibly small.

Ion beam stitching

Ion beam stitching of Cu(70 nm) on clean as-cast Teflon surfaces [3] was successful (30 g/mm peel strength), using low doses of He^+ or Ne^+ ions, as shown in **Figure 7(a)**. At doses above $3 \times 10^{15}/cm^2$, failure began to occur within the polymer, evidently structurally weakened by radiation damage. Such a limitation exists for most polymers.

Pre-sputtering

Low-energy ion pre-sputtering of the polymer not only avoids subsurface radiation damage to the polymer; it is also far more effective in producing a high-strength (and thermally stable) bond (75 g/mm), as reported by Chang et al. [28] [see **Figure 7(b)**]. As a practical technique, this is especially attractive, since only a few seconds' exposure to the ion source produces maximum adhesion. It was also found that the irradiated Teflon surface does not lose its capacity to bond with deposited Cu after several minutes of air exposure; the process step is therefore very tolerant. Longer exposure to the ion beam produced a high degree of roughening of the Teflon surface. However, the adhesion evidently does not depend on this effect so much as on the generation of active bonding sites at the substrate surface. Ingemarsson et al. [29] used XPS and CEMS to identify the bonding condition of Fe deposited on a Teflon surface following ion bombardment *in situ*. Their CEMS data are displayed in **Figure 8(a)**, which shows the ion dose dependence of the relative intensity of spectral components that represent, respectively, metallic Fe, Fe–C bonding, and Fe–F bonding at the interface. **Figure 8(b)** shows their XPS data that document the corresponding changes in interface carbon bonding. The figure plots intensities of C 1s constituent peaks that correspond respectively to the original CF_2, carbon in fluorine-rich surroundings (CF_3), and carbon in fluorine-depleted surroundings (CF + C + graphite). The

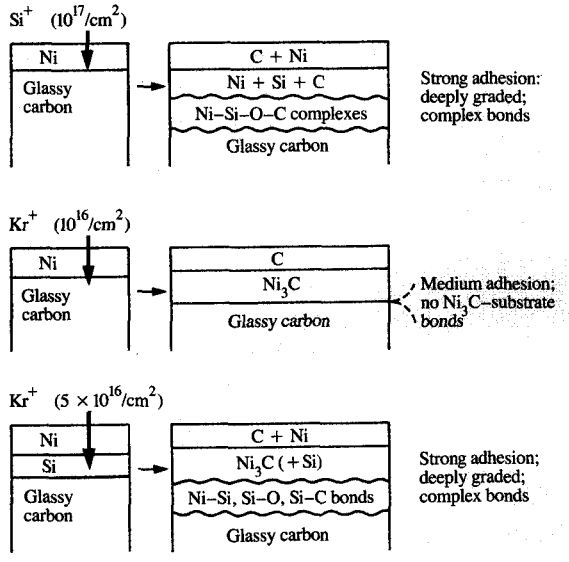

Figure 6

Ion implantation and ion beam stitching to assist adhesion of Ni on glassy carbon. Galuska [26] found good adhesion to be correlated with complex chemical bond formation at the interface.

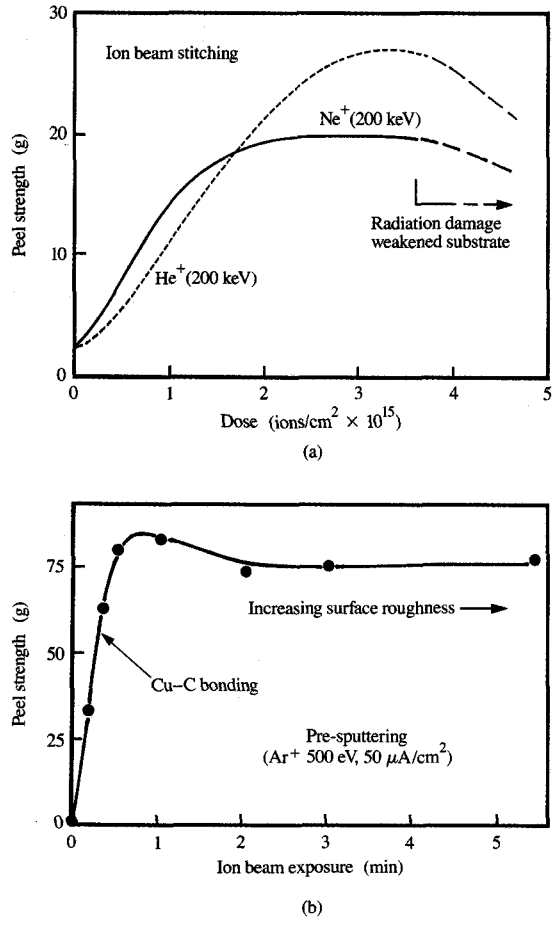

Figure 7

Adhesion of Cu(70 nm) on Teflon: (a) Ion beam stitching. (b) Pre-sputtering of the substrate with 500 eV Ar^+ ions (50 $\mu A/cm^2$). (From reference [2], reproduced with permission.)

correlation between Figures 8(a) and 8(b) supports a model of replacement of C–F bonds by C–Fe bonds, which are presumably responsible for the observed adhesion. The development of both scission and cross-linking was inferred for the Teflon surface (which may incidentally create a tougher surface layer).

Ion-beam-assisted deposition

Good adhesion of 40-nm Cu (or Au or Ag) films upon Teflon was obtained by Loh et al. [30], using bombardment with 400 eV Ar^+ ions (25 $\mu A/cm^2$), both prior to and during film deposition. The authors attributed the bonding to ion beam mixing by recoil of Cu into the Teflon during deposition, to create a graded joining layer.

- *Reactive ion pre-sputtering*

The admixture of oxygen ions with Ar^+ for low-energy *in situ* pre-sputtering of a substrate has been shown to benefit adhesion in several cases. Erck et al. [31] treated Al_2O_3 in this way prior to depositing silver films. Ar^+ ion sputtering alone produced good adhesion; however, the bonding was greatly enhanced by the addition of oxygen. Similarly, Kinbara et al. [32] found improvements for bonding Au on Teflon after addition of oxygen ions in the pre-sputtering beam.

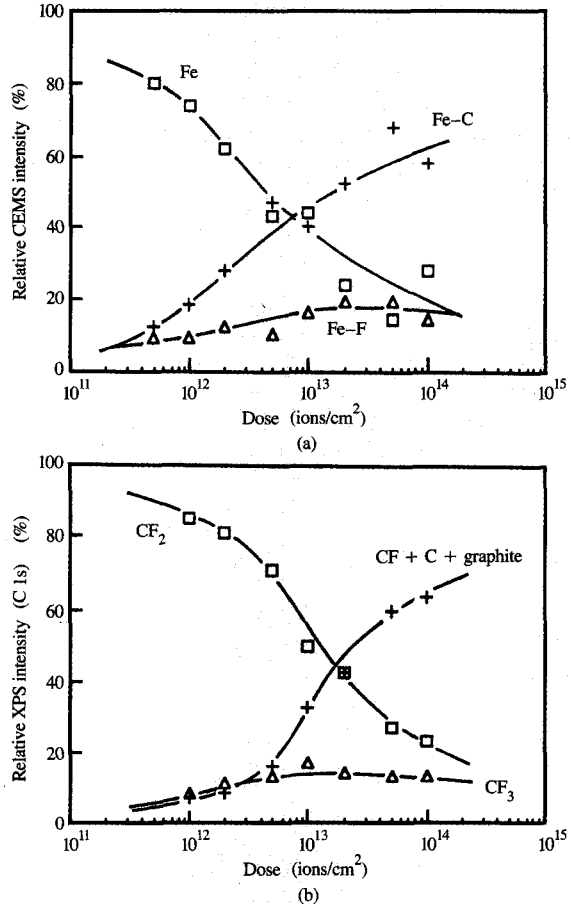

Figure 8

Chemical bonding resulting from ion beam stitching (16 MeV S^{3+}) of Fe on a Teflon surface: (a) Relative amounts of Fe bonding states in the interface 2-nm layer, as a function of ion dose, as inferred from CEMS data. (b) Relative amounts of C bonding states at the interface, as inferred from XPS data. (From reference [29], reproduced with permission.)

• *Electronic processes in stitching*

Some early discussion of ion beam stitching attempted to attribute its success either to the purely electronic energy loss of the ion in the interface region or to the ballistic recoil ("nuclear") energy loss components [33, 34]. Since both contribute to the net energy available for interface mobilization, it would seem that neither mechanism alone is responsible. However, a recent experiment by Wang et al. [35] clearly shows that electronic energy deposition alone can be fully responsible for ion beam bonding. (See **Figure 9**.)

Wang et al. used 0.4–2.5 GeV Bi ions to bond Cu on Teflon, achieving a peel strength of 28 g/mm. At that energy, the ion energy loss is all electronic, yet the adhesion obtained matched that recorded for 200 keV Ne^+ bombardments (where collisional energy loss is dominant).

An electron beam alone can, in fact, produce effective adhesion enhancement. Hull et al. [36] used 10–30 keV electrons to improve markedly the bonding of Au(90 nm) on glass, and found the best result to correspond to the electron energy for which the largest specific energy loss occurred at the interface.

These successes should not be taken to indicate that electron irradiation would normally be technically preferable to ion beam processing. Sample heating problems and long irradiation times result from the need for large electron doses, making processing difficult.

• *Applications*

Composites

Recent work by Grummon et al. [37] has shown the potential for ion-assisted adhesion as a tool for controlling internal bonding in fiber composites. They activated the surfaces of fibers by N^+ or Ar^+ bombardment prior to their embedment in epoxy. Polyethylene fibers thus treated showed a fourfold increase in interfacial strength, attributable to an increased density of surface functional groups. In contrast, Kevlar® fibers performed poorly due to loss of tensile strength of the fiber. Nevertheless, ion processing appears to offer a powerful option in future custom-tailoring of composites.

Lithography

It is worth noting that the kind of low-dose ion beam irradiation required for thin film bonding (especially low-energy pre-treatment of substrates) is readily adaptable to lithographic applications, using either masks or microbeam writing. In such a case, the irradiated and adhering area of a coating will remain attached to the substrate, while the untreated region can be removed by various lift-off processes. The ion beam technology is now so well understood, and so readily available, that such applications as selective-area film deposition seem ripe for adoption today.

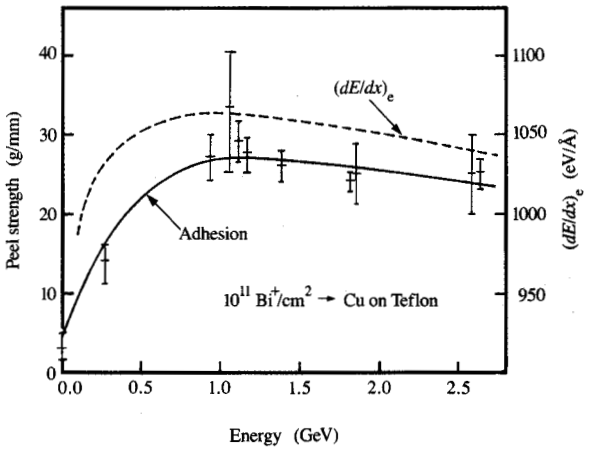

Figure 9

Role of electronic energy deposition in ion beam stitching. Enhanced adhesion for Cu on Teflon is shown to be substantial for GeV Bi^+ ion bombardment (where virtually all energy transfer is electronic); the adhesion is shown to track with $(dE/dx)_e$ at the interface for various ion energies. (From reference [35], reproduced with permission.)

Conclusion

Ion beam techniques for enhancing or creating adhesion of thin films are in general well understood and readily accessible. Their use can simplify multi-step manufacturing processes, and can provide reproducibility and control in materials processing, and bond integrity and durability in the products.

Interface chemistry induced by the ion beam processing provides the principal adhesion mechanism, even for bulk-incompatible systems. However, some systems will require the controlled addition of a reactive species, which can be done by ion implantation or ion mixing.

Ion-assisted adhesion can result from tailoring only one or two monoatomic layers at the film–substrate interface. As many technologies begin to depend on smaller dimensions and thinner films, the adoption of ion beam tailoring would seem to be increasingly appropriate and beneficial.

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Received December 9, 1993; accepted for publication May 10, 1994

John E. E. Baglin *IBM Research Division, Almaden Research Center, 650 Harry Road, San Jose, California 95120 (BAGLIN at ALMADEN, baglin@almaden.ibm.com).* Dr. Baglin is a Research Staff Member and manages the Materials Physics Group in the Physical Science Department at the Almaden Research Center. He received B.Sc., M.Sc., and Ph.D. degrees in physics from the University of Melbourne, Australia, in 1957, 1959, and 1963, respectively. He subsequently taught for four years at Iowa State University and six years at Yale University, before joining IBM in 1972. He conducted research in thin film interactions, radiation effects in solids, and ion beam analysis at the Thomas J. Watson Research Center, and in 1988 he moved to Almaden to establish new programs there in ion beam analysis and materials physics. Dr. Baglin received IBM Outstanding Technical Achievement Awards in these fields in 1982 and 1988, and an IBM Research Division Award in 1979. He is the author/editor of 13 book chapters/books in these topics, including several on the basics of interface adhesion. He is a Fellow of the American Physical Society, a former President of the Materials Research Society, a member of the Materials Education Council, and a member of the Editorial Advisory Board for the *Journal of Adhesion Science and Technology*.