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FOCUSING ON SURFACE RELATED ASPECTS OF MATERIALS SCIENCE

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EDITORIAL NOTES

During the week of November 7, 2005 MST CONFERENCES will be holding the 4th in its series of symposia on Polyimides and High Temperature Polymers along with the 2nd International Symposium on Adhesion Aspects of Thin Films in Savannah Georgia. Apropos of this event, this issue of the Newsletter will be focusing on these two topics and their interrelation. The following narration gives some reminiscences of our

experiences with these topics as they played out in the mainframe computer business during the late 1970' s and 1980's.

Polyimides, Stress and Adhesion: or There are no Bad Materials, Just Bad Uses of Good Ones:

Prelude to polyimides as electrical insulators

Subsequent to the DuPont company's patenting of the polyimide materials, one of the first major applications was for electrical insulators capable of

sustaining high temperature conditions. To those of us who were first exposed to the properties of engineering thermoplastics in the 1950's, the polyimide materials were a marvelous revelation. Those who recall the early days of manufactured goods made of plastic materials will remember that if subjected to high temperatures, say the flame from a match, these items would either melt into a viscous goo or possibly also ignite and burn. In addition, articles made from the early resins were highly prone to fracture as in the case of children's toys made from polystyrene. On the positive side, however, the early plastics were very easy to process into a large variety of useful shapes by either molding or casting methods. Thus one could easily and very cheaply manufacture useful household items such as knives, forks, cups and spoons. So cheaply in fact that these became throwaway items. One could even get around the brittleness problem by using polycrystalline materials such as polyethylene or polypropylene. These resins could be drawn or extruded into flexible sheets or tubing for use in packaging or plumbing applications. However, these materials also had the problem of temperature stability and would either distort or melt at temperatures at or above 100C.

Thus it seemed that the price one paid for low cost and ease of manufacture was limited thermal-mechanical performance. Now, however, along came the polyimide materials which were clearly polymeric in nature but which also possessed extraordinary thermal stability previously unheard of in a polymer. The earliest polyimide to be produced in commercial quantities was the KAPTON^{®1} film material made by the DuPont company. Here was a flexible plastic film that you could take a match to and it would not burn or melt. Under a nitrogen environment this material could be shown to be stable up to 400C in a Thermo-Gravimetric (TGA) experiment. This was truly astounding behavior for a polymer and it was felt that here was a class of materials that could surmount the thermal-mechanical limits of the ordinary thermoplastics. However, high performance came at a price. It turned out that in order to process the KAPTON material one had to use concentrated sulphuric acid or some other equally potent solvent. It seemed there would be no free lunch. If you wanted the high performance

¹ The basic resin goes under the name pyromellitic dianhydride oxydianiline or PMDA-ODA for short.

thermal-mechanical properties you had to sacrifice ease of processing.

All was not lost though since there was another way to make polyimide films without resorting to extreme processing techniques. It turns out that nearly every polyimide has a twin sister known as a polyamic acid. The polyamic acid has a chain architecture very similar to its polyimide sibling except that instead of the refractory imide group one has an acid moiety which gives the chain much more flexibility and also makes it much more soluble in relatively benign solvents such as N-methyl-pyrrolidone (NMP). Thus one first casts a film of the amic acid material out of NMP and then after drying the amic acid can be converted to the polyimide by curing at an elevated temperature. With this processing strategy it seemed as though the ultimate miracle had finally been achieved. Now one had a relative simple and benign process for achieving high performance films and coatings.

It was at this stage in the late 1960's and early 1970's that the microelectronics industry started to take a serious interest in using the polyimide materials as high performance insulators for semiconductor devices and advanced multichip modules. Up to that time the insulating material of choice was sputtered glass. This material is essentially amorphous SiO₂ which is the purest form of glass known and forms the basis of nearly all glass artifacts. The glassware in your cupboard is basically SiO₂ doped with boron and other materials which are used to give the final artifact a number of desired properties such as color, density, ... etc. SiO₂ was also a natural for the microelectronics industry since nearly every silicon wafer comes with a thin layer of SiO₂ due to the natural oxidation behavior of the pure silicon. This thin oxide layer is the primary reason that silicon is the primary semiconductor material used for microchips in the world today even though one can in principle use materials such as gallium arsenide to make significantly faster devices. Gallium arsenide does not come with a built in insulating layer whereas the oxide layer on the silicon serves as a convenient and highly efficient built in insulator which is crucial to the manufacture of integrated circuits. All circuits require three separate materials: a semiconductor, a conductor and an insulator each of which is critical in fabricating the final device. By chance SiO₂ came as a made to order insulator on top of every silicon wafer which could be used as is or enhanced in thickness for wiring up transistors and other devices into integrated circuits.

Amorphous SiO₂ was indeed a wonderful insulator material but it came with its own set of drawbacks which became painfully apparent as soon as one wanted to make multilevel structures. Among the list of problems with using SiO₂ were that such coatings were subject to pin hole defects if they were too thin and if too thick they were susceptible to cracking also. However, one of the biggest problems was the fact that SiO₂ coatings were conformal, i.e. they closely replicated the underlying surface. This is a killer issue when making multilevel circuits. The first level is no problem since one is building on top of a flat silicon wafer. After the first layer is built it has a complex topology of metal lines and other structures which need to be covered over before the next layer can be built. This is where the problem with SiO₂ starts, since after coating, all of the hills and valleys of the underlying circuitry will be replicated leaving a lumpy surface. This surface must somehow be flattened before the next layer can be built. One would much rather have a coating that filled in all of the hills and valleys leaving a completely flat surface the same way that water filling a rough basin leaves a perfectly flat surface regardless of the topology of the underlying lake bed. In the jargon of the industry what one wants is a planarizing coating material that will leave behind a flat smooth surface.

Enter the polyimide materials. Since these materials go down as a viscous liquid, they tend to planarize the underlying topology much better than SiO₂. The degree of planarization is not perfect but is nonetheless much much better than what one gets with SiO₂. Thus it looked as though the polyimides were a natural to replace SiO₂ as the insulator of choice for multilevel circuits, since not only did they planarize much better they also had a significantly lower dielectric constant which for the circuit designers meant that one could go to higher wiring densities before the problem of crosstalk between metal lines became a problem. Thus it was that in the early to mid 1970's very serious development efforts got underway within the microelectronics industry to use the polyimides as replacement materials for SiO₂ in multilevel wiring structures. It was also at this time that the staff of MST got their first exposure to the polyimides and the host of problems that came along with them.

Professor J. E. Gordon has neatly summed up the nature of dealing with new materials in this insightful comment: "A deep, intuitive

appreciation of the inherent cussedness of materials and structures is one of the most valuable accomplishments an engineer can have. No purely intellectual quality is really a substitute for this"². We were about to learn the truth of this of this statement firsthand as we started upon a development program to use the polyimide materials as insulator layers in multilevel wiring structures. But first a little introduction to the essential architecture of mainframe computers.

Wiring needs of a mainframe computer

All digital computer devices are what might be called "vertically integrated". That is they form a layered structure. At the lowest level, the basic calculations and data manipulations are carried out by transistors, diodes and resistors on silicon chips at the scale of roughly 1 micrometer and for the most advanced devices less than half that dimension. This is referred to as the chip level. A problem immediately arises due to the fact that humans cannot directly read data stored at the 1 micrometer scale. The digital signals must be scaled up to a coarser size or in technical jargon fanned out in order to be interpreted. The way this is done is to package the silicon chip on a larger substrate, typically but not necessarily a ceramic block, where the wiring structure is fanned out to roughly 100 times the dimension that exists on the chip. This is the second layer commonly referred to as the second level of wiring or the first level of packaging. If this is still not enough, yet a third level of wiring is employed in a third layer whereby the ceramic block is plugged into an epoxy based board which fans out the wiring density another 10 to 100 times. By this stage one usually achieves a wiring density that can be dealt with by human fingers which can then plug the wires into useful devices such as disk drives, display screens and keyboards. The polyimide materials were being considered for application at both the first and second level of wiring and this is where the story starts to get interesting. First, however, we need to digress briefly on the overall architecture of mainframe computers.

In the late 1960's and early 1970's the IBM company was having great success packaging single chips on ceramic substrates roughly 3/4" square. These ceramic modules would then be

² "Structures or why Things Don't Fall Down", J. E. Gordon (Da Capo, Press, 1978) p. 63

plugged into epoxy boards which could further be mounted into racks which would then constitute a mainframe computer. This was all well and good but there was still much room for improvement. In the first place all those cards and boards mounted in racks were large messy affairs taking up a lot of room and requiring extensive support structures such as cooling fans and power supplies. Another even more serious problem was the fact that by mounting each chip on a single ceramic module one was setting up a communications barrier of sorts between the chips. For example, say that a central processing circuit on one chip needs a piece of data on a remote memory chip. The electrical signal which transfers the data has to go from the chip to the ceramic module, thence to the supporting card, from there to the ceramic module supporting the memory chip and then to actual chip itself which sends the desired data back by the same route. It quickly became apparent to the electrical designers that the main bottleneck standing in the way of improving machine speed was the highly spread out packaging structure which single chip modules required. One idea that came up was to make the machine as one huge integrated circuit on a 3 inch wafer. This never flew for a number of reasons not the least of which was the problem of doing 1 micrometer lithography accurately over a span of 3 inches. The next level of thinking said that if we cannot cram the whole machine onto a single wafer at least we can mount all the chips on a single substrate and thereby eliminate one full level of packaging. At this stage the concept of a multichip module was born. Not only that, this concept was vigorously implemented resulting in multichip ceramic modules with approximately 40 levels of wiring buried in the ceramic and supporting up to 100 chips. It is hard to convey just how successful this multichip module concept was. By eliminating one full level of packaging the IBM company was able to manufacture machines in the early 1980's using chip technology that had been fully developed and amortized by the mid 1970's. These machines were cheaper than and out performed those of competitors which were using the latest expensive chip technology in order to achieve similar performance. I think one can safely say that this technology made a major contribution to the roughly \$4billion/year profit that the company was earning in those days.

Implementing polyimides: or development programs always work out better in slide presentations than in the development lab

Part one: prelude to selecting a material

If it is true that in the fashion industry one can never be thin enough and in business never rich enough then in the computer industry one's machines can never run fast enough. Already in the late 1970's we were looking for ways to improve the performance of the large multichip substrates. The material being used at that time was essentially alumina (Al_2O_3) ceramic. This was the same material used for the single chip modules and was an industry standard insulator for all applications requiring stability at high temperatures. Its main strengths are its excellent insulating properties and outstanding thermal-mechanical durability. Its main weakness is its relatively high dielectric constant and its highly refractory nature which forces the use of equally refractory metals such as molybdenum as the embedded electrical conductor. This arises from the fact that the alumina and the chosen metal must be co-fired together in a furnace in order to achieve the final multilayered structure. Since firing alumina requires temperatures on the order of 2000 C only the refractory metals such as molybdenum can be used. Other metals such as copper and aluminum simply cannot take the heat!

From the electrical design point of view this was a double whammy both in terms of achievable signal speed and wiring density. As a rule of thumb the fastest and densest circuits are achieved by using a low dielectric constant insulator combined with a high conductivity metal. The alumina/molybdenum pair were quite mediocre performers on both counts. However, a solution to this dilemma quickly presented itself due to the dual electrical functions performed by the packaging substrate. At the most basic level the substrate has to provide power for all of the chips. The power signal does not have to be exceptionally fast and the requirement is readily met by the alumina/molybdenum combination. At the next level comes the signal wiring which must transfer data among all of the chips. The machine performance is critically dependent on the speed of this wiring and this is where alumina/molybdenum fails to make the grade. The resolution to the problem now pops out. Make the basic substrate out of alumina/molybdenum to handle the power requirements and then build thin film

polyimide/metal wiring on top to handle the signal wiring where the metal can now be a high conductivity material such as copper or aluminum.

The stage was now set for the polyimide materials to make a major contribution to high level packaging technology. All that had to be done was to select the appropriate material and make it work. In all of the group meetings and slide presentations it looked like a done deal. However, the cussedness of the real material world was about to enter the stage in a most decisive way.

The first step of course was to choose an appropriate polyimide material. This is a far more critical step than might be appreciated at first. There are essentially a near infinite number of polyimides to choose from depending on the details of the backbone architecture and any side groups that might be added. Nonetheless, a choice had to be made and made quickly since in the microelectronics industry any development program has to "hit the ground running" as the paramilitary people would put it. Requirement number one was that whatever material was going to be used had to be commercially available, which greatly pared down the field of choices. The final choice was made even easier since there was one polyimide that had already been experimented with at the chip level in making 1 micrometer thick insulator layers. This was a commercial product that went under the name "Skybond 703"[®]. The original application was apparently as a high temperature glue for high performance fighter aircraft. This material had all the desirable properties required of an insulator material including a low dielectric constant but most importantly it planarized very well. What cinched the case for the packaging laboratory, however, was the fact that this material already had a track record of sorts. Thus the program went forward to fabricate thin film wiring onto of ceramic substrates using the Skybond material. Everything looked fine since the only change being made was that 10 to 15 micrometer coatings would have to be fabricated instead of 1 micrometer layers which the chip people were using. Now how could simply making thicker coatings cause any problems?³

³ Answer: The tendency of coatings to crack and delaminate scales linearly with the coating thickness. This comes directly out of elementary fracture mechanics.

Part two: revenge of the material gods

In retrospect it is hard to believe that one could have found a worse material for the application at hand. In essence, had we systematically screened all of the polyimide materials and then on the basis of a rigorous analysis tried to select the worst possible material I doubt that we could have beaten the Skybond material. As far as I can remember not a single viable substrate was made. The coatings all had massive cracking problems due to a number of thermal-mechanical problems that went entirely overlooked. The first problem was that Skybond had nearly all the mechanical properties of window glass. The strain at break was less than 2% and if you looked at a typical stress-strain curve and suppressed the scales on the axes the diagram was indistinguishable from that which a glass sample would give. This by itself does not necessarily imply disaster since many glue type materials are mechanically brittle but still perform adequately. However, the second problem that descended was the fact that the thermal expansion of the Skybond material was some 10 times larger than that of the ceramic onto which it was coated. This should have set off alarm bells since, as mentioned above, the polyimide materials have to be cured at an elevated temperature which in the case of Skybond was roughly 400 C. Oh Oh, could be trouble ahead. A little arithmetic immediately reveals that on cooling from the curing temperature at 400 C to room temperature at 20 C the part in question will have undergone a thermal excursion of roughly 380 C which, when multiplied by the thermal expansion difference between the polyimide and the ceramic, gives rise to a rather substantial thermal strain. There is a handy little equation called the membrane formula which allows one to quickly estimate the expected stress level in a coating which is subjected to these process conditions. In a nutshell it goes like this:

$$\sigma = E \times \Delta\alpha \times \Delta T / (1 - \nu)$$

In this equation E is the modulus of the polyimide, $\Delta\alpha$ thermal expansion difference between the polyimide and the ceramic, ΔT the temperature excursion and ν Poisson's ratio of the polyimide. In this example $E = 3\text{GPa}$, $\nu = 1/3$, $\Delta\alpha = 30 \times 10^{-6}/\text{C}$ and $\Delta T = 380\text{ C}$. Inserting these values into our little formula gives an expected biaxial stress of $\sigma = 0.051\text{ GPa}$ (GigaPascal) or in more convenient notation 51 MPa (Megapascal). Now what does this value 51 MPa mean? Looking at a stress strain diagram for Skybond one immediately

notices that the ultimate tensile strength of the material is close to 70 MPa. Thus upon coating Skybond onto a ceramic substrate and curing at 400 C one has a uniform coating that is already stressed to about 3/4 of its ultimate breaking strength. Not enough to cause a problem you say. This is true. The properly fabricated blanket coatings almost never gave a problem. Unfortunately one cannot stop at a blanket coating. One also has to drill via holes in the film and fill them with metal in order to electrically connect to the wiring below. However, by doing so one creates what is known as a stress riser or point of stress concentration. A fairly elementary analysis demonstrates that close to such a hole the local stress field increases by a factor of 2 to 3 which automatically puts the stress level over the top for Skybond.⁴ This was in fact what was observed in all cases. As soon as the parts emerged from the plasma etcher where the via holes were bored, ubiquitous radial cracks were observed emanating from nearly every via structure. In fact nearly any kind of imperfection in the coating such as particle contamination or a defect in the substrate would also act as a stress riser and thereby give rise to cracking of the polyimide.

Part 3: revenge of the adhesion gods

OK, so we learned that it was not a good idea to go with a brittle material and maybe also we would have to pay more attention to the thermal mechanical properties of the polyimide as well as its planarizing properties and whether or not it is commercially available. Quite after the fact I looked into the history of the development process and thereby came across a memo describing the material property selection criteria. In this document was a table listing about a dozen different polyimides along with columns specifying their electrical properties, how well they planarized, whether they were commercially available ... and so on. There was only one column listing a thermal-mechanical property and that was the thermal expansion coefficient. However, the memo went on to point out that,

⁴ A detailed discussion of the stress state near a via hole can be found in the following: "Stresses in thin Polymeric Films: Relevance to Adhesion and Fracture", Robert H. Lacombe in Surface and Colloid Science in Computer Technology, Ed. K. L. Mittal (Plenum Press, New York, 1987) p.179

since all of the polyimides listed had roughly similar thermal expansion coefficients, this property would thereby not be considered. Oh well, at least someone was starting to worry about the thermal-mechanical properties of the polyimide but somehow could not quite make a case for paying close attention to this detail. This was hardly surprising since in the early days of the program the entire team consisted of either chemists or electrical engineers who were really not in a position to appreciate the subtleties of stresses in thin films.

Moving right along, it quickly became clear that using a brittle material was not going to work and as soon as someone familiar with the mechanical properties of polyimides was brought on board it was pointed out that there are mechanically tough materials available. In fact the PMDA-ODA material which forms the basis of the KAPTON films mentioned above was one such material. Unlike the other polyimides which were essentially amorphous materials the PMDA-ODA material was quasi crystalline in that it had an ordered liquid crystalline type of morphology due to the length and rigidity of the backbone repeat unit. The stress strain diagram of this material looks almost like a rubber with a strain at break approaching 100% or better. It is the semi-ordered morphology that explains the toughness of the material. If you have an amorphous glassy material like the standard polyimides, and you apply a tensile load to it, there is not much that the material can do to accommodate the applied load. The induced stress in the material must be supported by the inter-chain van der Waals attractive forces and these are not very strong and are very short range to boot. Thus one gets a very low strain at break. With the PMDA-ODA material, however, the initial effect of the applied load is to start pulling apart and stretching out the semi-crystalline phase and only after this is accomplished does the load shift entirely to the inter-chain bonding forces. This effect is most dramatic in polycrystalline polymers such as polyethylene which can stretch out to 200% or better.

Thus, by going over to the PMDA-ODA material the problem of mechanical cracking was eliminated but unfortunately the thin film stresses remained since PMDA-ODA has roughly the same thermal expansion behavior as the other polyimides. The immediate consequence of this was that instead of cracking the material delaminated. The gods of adhesion now extracted their revenge. Coating

PMDA-ODA on nearly anything such as silicon or SiO₂ tends to give poor adhesion due mainly to the chain rigidity, limited scope for chemical interaction and the pervasive presence of high residual stress levels. Thankfully, the chemists were now able to step in and alleviate this problem with the use of coupling agents such as the silane materials. The silanes improved the adhesion of PMDA-ODA tremendously and allowed the program to progress to the point where thin films with full via structures could be fabricated.

Part 4: Twilight of the polyimide program

I would like to report that at this stage the program went forward ending in a triumphal success. However, this was not to be. Development programs involving advanced materials technologies are complex and chaotic processes and the final result tends to be determined as much by luck and circumstances as by engineering skill and design expertise. Too much time and resources had been dissipated with too little in the way of results coming out of it. In addition, an even more ominous threat came onto the scene. The ceramics group which had developed and implemented the alumina based technology was not standing idly by. They essentially came upon a ceramic material which could be sintered at under 1000 C and thus could be co-fired with copper. Not only that, this material also had a low dielectric constant. Thus coupling a low dielectric constant with a high conductivity metal the electrical designers could easily show that an all ceramic/metal module was possible with greatly improved signal speed and wiring density. Two other circumstances, however, were what really sealed the fate of the polyimide program. The major circumstance was essentially political. The ceramics group was essentially the party in power having already developed and implemented the alumina/molybdenum technology and as a consequence held most of the positions of authority and clout within the organization. The second circumstance which provide the "coup de grâce" was the fact that the limited resources available allowed only one program to go forward. Thus ended the polyimide program.

Epilog

As fate would have it the material and adhesion gods were just beginning to show their wrath and were now about to truly demonstrate the cussedness of real materials. Whereas it was true that the new ceramic material had much better electrical properties than alumina, its thermal-mechanical properties were a disaster, even worse than Skybond. In order to achieve a low sintering temperature the new material had to have a high glass content and this essentially gave it all the properties of window glass. Worse yet, as is well known to all those who work with glass, it had very poor adhesion to copper. As a consequence cracking and delamination problems descended with a vengeance. In retrospect all of this could have been anticipated in advance but one always has to remember the chaotic nature of real world development programs. Time, resources and expertise were in very short supply and the need to press forward unrelenting. Leaving out the gruesome details, the ultimate consequence of these technology failures were truly tragic. For the multichip module program the critical upshot was that a technology which should have been delivered in 1985 did not materialize until approximately 1990. This is a 5 year delay which in the microelectronics industry amounts to an eternity. One can never afford that kind of delay. While the development lab was wrestling with the daemons unleashed by the material and adhesion gods, microprocessors and personal computers based on them were steadily advancing. These devices were selling for a few thousand dollars whereas mainframe computers were going for closer to a million. In order to be competitive the mainframe had to offer much greater computing power. A factor of 2 or 3 was not good enough since PCs were so cheap one could just let a few of them run overnight. No, the mainframe had to offer a bare minimum of at least a factor of 10 to 100 greater compute power. In essence the only way a customer is going to shell out mainframe level dollars is if the mainframe would handle work loads the PC's could not. One had to deliver what is called an "enabling" technology. One that could deliver what the competition could not. If we could have delivered the advanced multichip module technology in 1985 as planned then mainframes 100 times faster than PC's would have emerged. Delaying the technology for 5 years made that dream impossible.

Ending on a more upbeat note, the polyimide materials have nonetheless done rather well in the

electronics industry as a whole. In particular they have found widespread use in flex circuitry whereby integrated circuit modules are mounted directly onto a flexible polyimide film similar to the KAPTON material mentioned previously. All of the wiring is electrodeposited copper which can be made to adhere very well to polyimide and, since everything is flexible, problems with cracking are avoided as well. This technology has found widespread use in everything from CD Players to ink jet print heads.

In closing it is appropriate to reiterate what I believe the universal theme of this essay "there are no bad materials only bad uses of good ones". All materials are essentially indifferent to our needs and aspirations, they obey the laws of physics and chemistry very rigidly and that is that. Any material whatever can find successful application so long as we understand its inherent nature and physical limitations. The Skybond material works quite well as a high temperature glue so long as you understand its limits. Developing such an understanding for polyimides and other high temperature polymers is one of the major goals of the upcoming MST symposia on HIGH TEMPERATURE POLYMERS and ADHESION ASPECTS OF THIN FILMS. Details of these symposia are given at the end of this newsletter. The staff of MST cordially invite all our readers to participate in either or both of these programs. In addition, at the end of the symposia MST offers a short course on ADHESION MEASUREMENT METHODS. This course addresses many of the fracture mechanics and stress related problems which so confounded the polyimide program. Remember, in a chaotic world one can never know enough about what is governing the materials and process we all have to deal with.

BOOK REVIEWS

Handbook of Adhesion, Second Edition, D. E. Packham, Ed., (John Wiley & Sons, Ltd, Chichester, UK, 2005) 638 pages

Prof. Packham presents us with an impressive volume covering nearly every aspect of the science of adhesion. The volume contains some 250 articles written in collaboration with over 60 contributing experts in the field. The format is that of a small encyclopedia with all of the articles suitably cross referenced so that the reader can easily track down relevant information by systematically jumping from article to article. Due

to the wide scope of coverage the individual articles are necessarily short and of limited depth. However, numerous references to the technical literature allow the interested reader to pursue whatever subject is of interest in more detail. Just a brief scanning of the articles quickly reveals just what an immense range of topics are covered within the realm of adhesion science. The list encompasses nearly all aspects of materials science from surface analysis to mechanics of materials to synthetic methods for adhesive manufacture. A detailed listing would require much more space than is available for this short review but one of my favorite articles is the review of "Adhesives - historical perspective" by M. W. Pascoe. The whole topic of adhesives and adhesive technologies is quite likely the largest subject area covered as it involves not only the interfacial aspects of adhesive/substrate interactions but also the synthesis and thermal-mechanical properties of the adhesive materials themselves. In addition the fracture mechanics and testing of adhesive joints could easily take up the entire volume if gone into in detail. What the reader will find most interesting in Dr. Pascoe's article is the fact that adhesive technology is by far mankind's first encounter with problems of adhesion. Archeological studies have apparently established that stone and bone points were apparently glued to wooden shafts during the paleolithic era (10 to 40 thousand years ago) using naturally available adhesives such as pine pitch and dandelion sap. The problems encountered then were much the same as those that crop up today concerning the best methods of forming the adhesive joint and the ultimate durability and serviceability of the finished artifact. Some things never change.

One of the more interesting topics dealing with ancient adhesive technology is whole field of restoring and preserving historical artifacts such as paintings and furniture that has been glued. One finds art objects where the adhesive has degraded over time and has to be removed. A specific case is that of removing the animal glues used to adhere Old Masters to acidic back boards in order to prevent harmful deterioration. Thus we see the science of adhesion intruding into the nominally liberal art of historic preservation and restoration. Adhesives and adhesive technologies moved into the modern era with the advent of synthetic adhesives such as the epoxies and the acrylates. Previously adhesives were very much a cottage industry and a semi-secretive craft which made quality control difficult. Industrialization

essentially forced suppliers to adopt more scientific production methods and to subscribe to rigorous manufacturing standards.

In conclusion we can highly recommend this volume as a handy and comprehensive overview of the many facets of adhesion science and technology. The contributing authors are among the leading experts in their respective specialties with international reputations. Dr. Packham is to be congratulated on assembling such a wide range of experts on a subject that has truly universal application and appeal.

Adhesion Aspects of Thin Films, Volumes I and II, Ed. K. L. Mittal; (Vol I: VSP, Utrecht, 2001, 270 pages), (Vol II: VSP, Utrecht, 2005, 232 pages).

Since MST will be holding the third in the series of ADHESION ASPECTS OF THIN FILMS symposia this November in Savanna, Georgia it is apropos at this time to review the proceedings of the first and second symposia. The first symposium was held in Newark, New Jersey in the Fall of 1999 and the plan was to hold subsequent symposia every two years. This automatically scheduled the second symposium for the fateful Fall of 2001 and in consequence of the tragic events in New York City that symposium had to be canceled. The second symposium was eventually held in December of 2003 in Orlando, Florida. Hopefully, if all goes well, the third symposium will take place this November.

As pointed out in the lead essay of this newsletter, the adhesion behavior and thermal-mechanical properties of the materials one is dealing with can have a very dramatic impact on the structures one is trying to fabricate. A number of issues come forward which are especially relevant to thin films including:

- Interfacial interactions governing the coating process.
- Buildup of stress in the coating with increasing thickness.
- Dependence of coating morphology on deposition conditions including substrate temperature and the presence of defects and contamination layers.

- Thermal-mechanical mismatch between coating and substrate materials including elastic properties and thermal expansion behavior.
- Physico-chemical issues relating to surface free energies such as wetting and surface diffusion behavior.

All of these issues come to bear on my favorite thin film adhesion topic which is the coating of diamond onto ferrous metals. This is one arena which is very jealously guarded by the material and adhesion gods. The inventor who can successfully coat thick layers of polycrystalline diamond onto mild steel will achieve a prize far more valuable than vaunted "Ring of the Nibelungs"⁵ At a very minimum the machine tool industry would be revolutionized by making available cutting tools with the toughness and strength of mild steel coupled with a hardness and cutting durability exceeding that of the refractory materials such as silicon nitride and silicon carbide. An immediate consequence would be the ability to easily and cheaply machine metal matrix composite materials which will wear out all but the hardest cutting edges in an instant. However, a number of formidable barriers stand in the way. In the first place diamond is nothing more than pure carbon but carbon diffuses readily into ferrous metal so unless one has a diffusion barrier in place one will never even grow the thinnest layer of diamond. This problem essentially comes under the physico-chemical heading mentioned above.

Assuming one can develop an appropriate barrier layer and start growing diamond films then the issue of increasing stress with coating thickness steps in. Past attempts at coating diamond on steel manage to make coatings about 2 micrometers thick before they pop off due to excessive stress levels. This problem falls largely under the category of thermal-mechanical mismatch between the coating and the substrate. Two papers in Volume I deal with the problem of diamond coatings for cutting tools. The first is "The State of the Art in Adhesion of CVD Diamond to Carbide Cutting Inserts" by M. A. Taher et. al.

⁵ For those unfamiliar with 19th century opera the Ring of the Nibelungen was a magical ring which would give fantastic powers to its possessor. It features prominently in Richard Wagner's "Ring Cycle" a collection of four massive operas written from 1853 to 1874.

and the second is "Adhesion Improvement of Diamond Films to Silicon Nitride Substrates for Cutting Tools" by H. Itoh et al. Both of these papers present state of the art studies in diamond coating technology as applied to the machine tool industry. The remaining papers deal with a broad range of coating technologies and cover all of the issues listed above.

Volume II continues in the vein of Volume I and adds to the topic of diamond coatings with a paper by D. J. Li and L. F. Niu on Diamond Like Carbon (DLC) coatings. DLC coatings represent something of a compromise in diamond coating technology. Instead of trying to achieve full tetrahedral symmetry (sp^3) polycrystalline coatings, one allows for a significant percentage of graphitic or planar (sp^2) material to be present. The advantage of doing this is that one can coat at much lower temperatures thus allowing materials such as plastics to be coated. The disadvantage is that one does not achieve the hardness and strength of full sp^3 diamond. However, DLC coatings are very hard and smooth with great potential for fabricating durable low friction surfaces. The paper by Li and Niu explores the biocompatibility of DLC coatings with blood and tissue with an eye toward developing low friction surfaces for bone replacement implants such as elbow, hip and knee joints. In addition Volume II has 5 papers dealing with the ever important topic of metallized plastics. This technology has wide ranging applications in lenses, automotive lighting and reflective coatings for plastic films. Again all of the issues listed above come to light in trying to achieve workable technologies.

Finally, Volume II includes 4 more papers dealing with the all important topic of adhesion measurement. The ability to carefully measure the level of adhesion of coatings is central to any development program that has to be concerned with adhesion durability. The papers presented deal with the ever useful and ubiquitous scratch test which is quite likely the most widely used test in industry especially for brittle coatings.

Polyimides and Other High Temperature Polymers: Synthesis, Characterization and Applications, Volumes 1, 2 and 3 (VSP, Utrecht) Vol 1, 2001; Vol 2, 2003; Vol 3, 2005.

This series of volumes is essentially a follow on to the first technical conference on Polyimides: Synthesis, Characterization and Applications which

was held under the auspices of the Mid-Hudson Section of the Society of Plastics Engineers at Ellenville, New York, in November 1982. This conference was documented in a 2 volume work by MST's director Dr. K. L. Mittal. The volumes contained a total of 71 papers (1182 pages) with contributions by 164 authors from nine countries and was published by Plenum Press, New York, 1984. These seminal volumes documented for the first time in a single format the tremendous amount of work that had been accumulating on polyimides ever since their introduction by the DuPont company in the mid 1960's. The volumes under review here continue in the vein established by this earlier work.

As the title of the volumes suggests, the papers tend to break down into one of three categories labeled as synthesis, characterization and applications. These topics all interact in a synergistic fashion. The synthesis of a particular polyimide will suggest an application and the needs of the application will demand careful characterization. Sometimes it works in the opposite direction whereby an application drives a program of synthesis of new materials which or course require further characterization. As alluded to in the opening essay, the electronics industry has been and continues to be one of the major driving applications for high temperature insulator materials. This industry also imposes the most stringent requirements for careful characterization. Examples abound. Take for example the need for a low dielectric constant in order to improve electrical performance. Garden variety polyimides give a dielectric constant of roughly 3.0 which is quite good for most applications and about half of what one expects from common ceramics. However, one always wants to go lower so one's circuits can go faster and this prompted the synthesis people to add fluorine groups to the chain backbone. Some fluorine containing polyimides attain dielectric constants near 2.0 which is a significant improvement. Thus we see an application need driving the synthesis process and it doesn't stop there since the new materials must be properly characterized. A dielectric constant of 2.0 is quite impressive but still a factor of two higher than the fundamental limit of 1.0 which can only be achieved by a vacuum. However, common air comes fairly close to this lower bound which suggests that making a polyimide foam would give a very low dielectric constant indeed. Such materials have in fact been fabricated and have found application in situations where light weight and high temperature are

critical such as in fire retardant insulators in aircraft.

Another important class of polyimides that were driven by the needs of the microelectronics industry are the photosensitive materials. Fabricating microcircuit devices requires the extensive use of photolithography in order to achieve very fine and carefully controlled structures. The standard approach is to first put down a blanket layer of the material which must be patterned. In this example we can think of a polyimide insulator on a silicon wafer with imbedded transistors and diodes which must be wired together in order to make useful circuits. Thus an array of via holes must be etched in the polyimide so that metal can be deposited to make electrical connection to the underlying devices. Step one involves coating over the polyimide with a photoresist material which can be optically imaged and developed in order to create a mask which has an opening wherever a via hole is to be located. At the next step the structure might be placed in a reactive ion etcher which will etch away the polyimide material left exposed by the holes in the photoresist. The photoresist will also be etched but is thick enough to protect the polyimide in those areas where no via holes are wanted. Finally, with the etching process completed the remaining photoresist must be washed away leaving a now nicely patterned polyimide layer with via holes exactly where one wants them. It all works quite well but is nonetheless a complex, time consuming and expensive process. Is there a better way? Of course. What if the polyimide material itself was photo-imageable? In this scenario, after depositing the polyimide one then directly exposes it to light radiation through a photomask just as in the previous process. One can go with either a positive or negative resist approach. Taking the negative approach the photomask blocks the light only to those regions where a via hole is desired. The remainder of the coating is exposed to the radiation and thereby photocured or hardened making it resistant to the subsequent etching process which will then remove only the unexposed areas leaving behind the desired via hole pattern just as was achieved by the standard approach. The photosensitive polyimide thus acts as its own photoresist eliminating the need for the photoresist and thereby saving many process steps.

Developing low dielectric constant and photo-imageable materials just starts to scratch the

surface as to what can be done with the polyimide materials. Another expansive frontier for innovation lies in developing better ways of depositing blanket coatings. The standard method for polyimides involves first depositing a layer of precursor polyamic acid either by spin coating, spraying or doctor blading. This precursor coating must then be dried and cured at elevated temperatures which then introduces an unwanted residual stress in the material due to thermal expansion mismatch problems. The microelectronics industry had a neat idea in this regard. In the first place they would like to dispense with the spin coating and spraying since these steps involve the use of solvents which are messy and require cleanup and further invite inspection by OSHA and other government regulation agencies to be sure the solvents are being properly handled and disposed of. What the microelectronics industry wants is a totally dry process which not only will eliminate the need for obnoxious solvents but will also allow the parts being processed to remain in an ultra clean high vacuum environment. Wouldn't it be nice if we could vapor deposit polyimides in much the same way that metals are vapor deposited. The answer is yes. Polyimides can and have been vapor deposited. Not only that but they have been put down by plasma techniques and even as monolayers. Just about any method one can think of has been tried at one time or another.

The reader will find all this and more in the volumes under review. Better yet the upcoming FOURTH POLYIMIDE SYMPOSIUM to be held in Savannah Georgia this November will continue to disseminate the latest findings in the process. We invite all our readers to join us for what promises to be a most engaging meeting.

UPCOMING SYMPOSIA

PRELIMINARY PROGRAM: FOURTH INTERNATIONAL SYMPOSIUM ON POLYIMIDES AND OTHER HIGH TEMPERATURE POLYMERS SYNTHESIS, CHARACTERIZATION AND APPLICATIONS; To be held November 7-9, 2005 at the Hilton Savannah DeSoto Hotel, Savannah, GA

This symposium is the fourth in a series the first of which was held in Newark, NJ in 1999. As with its predecessors, this symposium will be concerned with all aspects of polyimides and other high temperature polymers. These materials have found

applications in such diverse areas as the aerospace industry and microelectronic components. A unique combination of physical and chemical properties make these materials highly attractive for demanding applications where chemical inertness, high temperature stability, low dielectric constant, mechanical toughness and processability are primary concerns.

This symposium is organized to bring together scientists, technologists and engineers interested in all aspects of high temperature polymers, to review and assess the current state of knowledge, to provide a forum for exchange and cross-fertilization of ideas and to define problem areas which need intensified efforts. The invited speakers have been selected so as to represent widely differing disciplines and interests, and they hail from academic, governmental and industrial research laboratories. This meeting is planned to be a truly international event both in geographic coverage as well as in spirit. The technical program will contain both invited overviews and contributed original research papers. It is planned to chronicle the transactions in a hard-bound volume of archival quality (to match or exceed the standards of the journal literature) which will serve as a reference work for future generations of investigators.

Listed below is a **partial list** of speakers for the planned program. Please note that the given address may only apply to the presenting author highlighted in blue.

SYNTHESIS

Ahmad Banihashemi, Bahman Tamami and **Amir Abdolmaleki**; Department of Chemistry, College of Sciences, Shiraz University, Shiraz, 71454, IRAN; **Synthesis and Properties of New Aromatic Polyimides Based on 2,2'-dibromo-4,4,5,5'-benzophenone Tetracarboxylic Dianhydride**

Zongwu Bai, Michael F. Durstock, Thom L. Reitz, Stanley J. Rodrigues and **Thuy D. Dang**; AFRL/MLBP, Materials Directorate, 2941 Hobson Way, Bldg. 654, Wright-Patterson Air Force Base, OH 45433; **Highly Sulfonated Polyarylenethioethersulfones As PEMs For Fuel cells: Synthesis, Characterization and Performance**

Hiroshi **Itatani**; PI R&D Corp. Ltd., 12-5 Torihama, Kanazawa, Yokohama, Kanagawa 236-0002, JAPAN; **Block Copolyimides soluble in Organic Solvents - Preparation, Catalysis and Properties**

Hiroshi **Itatani**; PI R&D Corp. Ltd., 12-5 Torihama, Kanazawa, Yokohama, Kanagawa 236-0002, JAPAN; **Different Behaviors in Preparation Processes Between Soluble Block Copolyimides Containing PMDA and Other Tetracarboxylic Dianhydrides**

M. S. Salakhov and A. A. Efendiev; Institute of Polymer Materials, S.Vurgun Str.124., Az 5004, Sumgait, AZERBAIJAN REPUBLIC; **Synthesis of Chlorinated Tri- and Tetracyclic Polyimide Ethers with Given Spatial Structure**

M. P. Srinivasan; Department of Chemical and Biomolecular Engineering, National University of Singapore, 4 Engineering Drive 4, Singapore 117576; **Covalent Molecular Assembly: Pathway to Robust Structures**

Arlen Valozhyn; Institute of Physical Organic Chemistry National Academy of Sciences, Minsk Institute of Electrical Engineering, ul.Sikorskiego 37, 70-313 Szczecin, POLAND; **Synthesis, Properties and Application of Cycloaliphatic Polyimides**

Hong-shen Li, Jin-gang Liu, Lin Fan, **Shi-Yong Yang**; Laboratory of Advanced Polymer Materials, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, CHINA; **Synthesis and Characterization of Novel Fluorinated Polyimides**

Bao-Ku Zhu; Institute of Polymer Science, Zhejiang University, Hangzhou Yuquan 310027, P. R. CHINA; **Imidization Process from Salt-like Precursors to Polyimides**

NANOCOMPOSITE TECHNOLOGY

B. Kouini and S. Fellahi; Polymer Engineering Department, Institut Algerian du Pétrole- CU, Sonatrach, Boumerdes, 35000, ALGERIA; **Compatibilizing Effect of Maleated Polypropylene on the Properties and Morphology of Injection Molded Polypropylene/ Polyamide6,6 Nanoclay Nanoblends**

Dale Danver and Tatiana Sukhanova; Sordal Inc., Holland, Michigan USA; **Very Low Density Polyimide Foam Incorporating Nanostructure Technologies**

Hiroshi **Itatani**; PI R&D Corp. Ltd., 12-5 Torihama, Kanazawa, Yokohama, Kanagawa 236-0002, JAPAN; **Recently Developed Applications of Polyimides: Photoelectro Devices, electro Deposition, Superconducting Tunnel Junction Devices and Polyimide Film dispersed Carbon Nanotubes**

H. Schmidt, E. Arpac . Gerdes, C. Becker-Willinger; Leibniz-Institute for New Materials, Im Stadtwald, Geb. 43 A, 66123 Saarbrücken, GERMANY; **Polyimide Nanocomposites Coating Materials with Special Functions**

Carey K. Bagdassarian, D. Scott Thompson, Luke M. Davis, **David W. Thompson**, and R. E. Southward; Department of Chemistry, College of William and Mary, Williamsburg, VA 23187; **Single-stage Near-surface Silver Metallization of Fluorinated Polyimides Yielding Reflective Nanoparticulate Hybrid Membranes at Low Metal Concentrations**

Jui-Ming Yeh; Chemistry Department, Chung Yuan Christian University, TAIWAN; **Organo-Soluble Polyimide/Clay Nanoaomposite Materials and Their Application as Advanced Corrosion Protection Coatings**

Vladimir E.Yudin; Institute of Macromolecular Compounds, Russian Academy of Sciences, V.O. Bolshoy pr., 31, 199004 St.Petersburg, RUSSIA; **New Results for Polyimide-Inorganic Nanocomposites.**

NOVEL MATERIALS/HIGH PERFORMANCE PROPERTIES

G. Gubanova, K Balík, M. Goykhman, A. Grigoriev, M. Černý, T. Sukhanova, V. Kudryavtsev, B. Ginzburg, D.tochilnikov; Institute of Macromolecular Compounds, Russian Academy of Sciences, Bolshoy pr.V.O. 31, 199004 St.- Petersburg, RUSSIA; **Polyimide's Binders for Carbon-Carbon Composites with Turbostratic Structure**

Kyung Hoon Lee, Seong Jun Lee, Seung Beum Lee, Kyung Ho Choi, Juhyun Park, Seong Oh Ham, Jin **Kook Lee**, **Gyo Jic Shin**, **Moonhor Ree** and **Jin Chul Jung**; Department of Materials Science & Engineering and Department of Chemistry, Pohang University of Science & Technology (POSTECH) San 31, Hyoja-dong, Pohang, 790-784 KOREA; **Synthesis of Novel Polypyromellitimides and Their Liquid Crystal Aligning Properties**

John D. Perry, P. Jason Williams, William J. Koros*; School of Chemical & Biomolecular Engineering, Georgia Institute of Technology, Atlanta, GA 30332; **Formation of Carbon-Polyimide Hybrid Materials for High Performance Separations**

Steve Shaw; Room 19, Bldg 231, Defense Sci. & Technol. Lab., Porton Down, Salisbury, Wiltshire SPA OJQ, UK; **Development of Ultra High Temperature Polymers**

A. Valozhyn, E. Schab-Balcerzak, B. Jarzabek, T. Chamenko, D. Sek; Institute of Electrical Engineering of Technical University of Szczecin, Sikorskiego 37, 70-310 Szczecin, POLAND; **Novel Optical Transparence Copolyimide Films**

Bao-Ku Zhu; Institute of Polymer Science, Zhejiang University, Hangzhou Yuquan 310027, P. R. CHINA; **Polyimide/ceramic Composites with Variable Dielectric Property in Large Range**

T. A. Aslanov, **M. S. Salakhov** and A. A. Efendiev; Institute of Polymer Materials, S.Vurgun Str.124., Az 5004, Sumgait, AZERBAIJAN REPUBLIC; **High Thermostable Polyethersulfimides Prepared by Polycondensation of Diethersulfimides with (1,3-dimethyl- 4,6)- and 1,4-Dichloromethylbenzenes**

T.E. Sukhanova, A.I. Grigoriev, V.M. Svetlichnyi, V.E. Yudin, G.N. Gubanova , G.N. Matveeva, A. Ya. Volkov, A. L. Didenko, V.V. Kudryavtsev, S. Ratner and G. Marom; Institute of Macromolecular Compounds, Russian Academy of Sciences, Bolshoy pr. 31, 199004 St.- Petersburg, RUSSIA; **Liquid Crystalline Textures and Crystallization Morphology in Aromatic Bisimides and Their Blends with Semicrystalline Polyimide**

ELECTRONIC APPLICATIONS AND CHARACTERIZATION

Hiroshi **Itatani**; PI R&D Corp. Ltd., 12-5 Torihama, Kanazawa, Yokohama, Kanagawa 236-0002, JAPAN; **Industrial application of Block Copolyimides: Posi- and Nega- Typed Photoresists, Adhesion, Electrodeposition, Crosslinked Low K, Films and Printed Photosensitive Materials**

L. Suboch, A. Valozhyn , N. Kamanina and N. Svidunovich; Institute of Electrical Engineering of Technical University of Szczecin Sikorskiego 37, Szczecin 70-313, POLAND; **Dielectrical Spectroscopy of Polyimide Films Doped by Fullerene**

P. Sysel, V. Sindelar , R. Hobzova , M. Frycova ,K. Friess ,V. Hynek , and M. Sipek; Department of Polymers, Institute of Chemical Technology, 166 28 Prague 6, CZECH REPUBLIC; **Transport Properties of Gases, Organic and Water Vapors Through Membranes Based on Polyimides**

F.Thominette, E.Gaudichet and J.Verdu; ENSAM, 151 Boulevard de l'Hôpital, 75013 Paris, FRANCE; **Water Sorption in Polysulfones: Water Solubility and Diffusivity**

N. Venkatasubramanian, Kevin J.Wiacek, Sandra Fries-Carr and Thuy D. Dang; University of Dayton Research Institute, 300 College Park Drive, Dayton OH 45469; **High Temperature Polymer Dielectrics For Capacitive Energy Storage Applications**

PRELIMINARY PROGRAM: SECOND INTERNATIONAL SYMPOSIUM ON ADHESION ASPECTS OF THIN FILMS (INCLUDING ADHESION MEASUREMENT AND METALLIZED PLASTICS); To be Held at the Hilton Savannah DeSoto Hotel, November 9-11, 2005

This symposium integrates key aspects of three symposia which were held separately in the past dealing with adhesion aspects of thin films, adhesion measurement and metallized plastics. The main idea is to provide a broader venue for the discussion and exploration of these three closely related fields of endeavor. The main part of the symposium is concerned with those aspects of thin film technology that have a direct bearing on film adhesion to the substrate. This is a topic of both fundamental interest to thin film technology

and of great practical concern in applications where films of high stress are involved. The coating of diamond films onto machine tools is one of many applications where thin films adhesion is a critical factor in coating durability. The second part of the symposium will deal with the ability to accurately measure the adhesion of coatings which is a crucial part of the development and manufacturing process dealing with coatings and films. Finally, metallized plastics are a burgeoning technology heavily dependent on thin film adhesion with applications ranging from decorative design to optical coatings to advanced thin film wiring schemes in the microelectronics industry. Metallized plastic films allow the technologist to capitalize on the favorable properties of two disparate classes of materials to create new and unique products which transcend the performance and usefulness that can be obtained by either class alone.

The invited speakers have been selected so as to represent widely differing disciplines and interests, and they hail from academic, governmental and industrial research laboratories. This meeting is planned to be a truly international event both in geographic coverage as well as in spirit. Below is a **partial** list of papers to be presented at this symposium. **Note:** the address listed is valid for the presenting author and may or may not be valid for the co-authors.

ADHESION ASPECTS OF METAL COATINGS

K. J. Belde and S. J. Bull; School of Chemical Engineering and Advanced Materials, University of Newcastle, Newcastle upon Tyne, NE1 7RU, UK; **Simulation of Adhesion Failure in Transit Scratches in Ultra-Thin Solar Control Coatings on Glass**

Y. H. Yan, **Mary B. Chan-Park** and C. Y. Yue; The Singapore-MIT Alliance Program (Innovation in Manufacturing Systems and Technology Program), Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798, SINGAPORE; **Electroless Nickel Deposition on Silicone-rich UV Micro-Embossing**

Maëllenn Aufray, **Alain André Roche**, Christophe Depecker, Daphné Merle and Marie-Geneviève Barthes-Labrousse; INSA de Lyon, Laboratoire des Matériaux Macromoléculaires (IMP/LMM), Bâtiment Jules Verne, 17 rue Jean Capelle, 69621 Villeurbanne Cedex, FRANCE; **Epoxy-amine / Metal Interphases: Influences from Sharp Needle-like Crystals Formation**

M. Charbonnier, **M. Romand**, and Y. Goepfert; Laboratoire de Sciences et Ingénierie des Surfaces, Bâtiment Raulin, Université Claude Bernard – LYON 1, 69622 Villeurbanne Cedex, FRANCE; **Ni or Cu Electroless Metallization of Polymer Substrates With and Without Pd-based Catalysis Processes**

Luke M. Davis, B. L. French, J. M. Compton, D. E. **Kranbuehl**, **D. S. Thompson**, **David W. Thompson**, and R. E. Southward; Department of Chemistry, College of William and Mary, Williamsburg, VA 23185; **Novel Route to Palladium Surface-Metallized Polyimide Nanocomposite Films**

ADHESION OF HARD COATINGS TO POLYMERS

Michel Ignat, Bruno A. Latella, Gerry Triani, Ken T. Short, John R. Bartlett; Laboratoire de Thermodynamique et de Physico-Chimie Métallurgique, associé au CNRS, E.N.S.E.E.G., BP 75, F-38402 Saint Martin d'Hères, FRANCE; **The Adhesion of TiO₂ and Al₂O₃ Thin Layers Deposited by Atomic Layer Deposition (ALD) on a Polycarbonate Substrate**

O. Knotek, K. Bobzin, E. Lugscheider, N. Bagcivan, and **A. Krämer**; Surface Engineering Institute, RWTH Aachen University, Augustinerbach 4-22, D-52062 Aachen, GERMANY; **Hard Coatings for Polymers**

B. A. Latella, M. Ignat, G. Triani, D.J. Cassidy and J.R. Bartlett; Materials and Engineering Science, Australian Nuclear Science and Technology Organisation, Private Mail Bag 1, Menai, NSW, 2234. AUSTRALIA; **Fracture And Adhesion of Thin Films on Ductile Substrates**

Omar Zohni; North Carolina State University, Mechanical & Aerospace Engineering, Cary, NC 27513; **Adhesion of PZT on Zr, ZrO₂, Ti, and Ta**

BIOLOGICAL SYSTEMS

A. Meyer-Plath, R. Mix, G. Kühn and **J. Friedrich**; Bundesanstalt für Materialforschung und -prüfung, Unter den Eichen 87, D-12200 Berlin, GERMANY; **Adhesion Aspects of Amino Functionalization for Attachment of Biomolecules and Adhesion-promotion of Copper Films**

F. Lewis, B. Maheux-Lacroix, S. Turgeon and D. Mantovani; Laboratory for Biomaterials and Bioengineering, Laval University, Quebec City, G1K 7P4, CANADA; **Development of a Method to Evaluate the Adhesion of Thin Polymer Films on Metallic Substrates for Long-term Stable Drug Eluting Stents**

R. Narayan, A. Doraiswamy, R. Cristescu, I.N. Mihailescu, N. Menegazzo, B. Mizaikoff, J.J. Wilker, I. Stamatin and D.B. Chrisey; School of Materials Science and Engineering, Georgia Institute of Technology, 771 Ferst Dr NW, Atlanta, GA 30332-0245; **Laser Processing of Mussel Adhesive Protein and Mussel Adhesive Protein Analog Thin Films**

P. K. Paul, S. A. Hussain and D. Bhattacharjee; Department of Physics, Tripura University, Suryamaninagar-799130, Tripura, INDIA; **Investigation of Miscibility in Guest-host Monolayer by Surface Pressure And Absorption Spectroscopic Study**

ENGINEERING DESIGN, MEASUREMENT AND STRESS

Monika Bubacz, David Hui and Leo Daniel; University of New Orleans, Department of Mechanical Engineering, New Orleans, LA 70148; **Different Solutions for Composite Sandwich Cryogenic Tank Design Using Coated Aramid Papers**

S. U. Jen; Institute of Physics, Academia Sinica, Nankangm Taipei, 11529 Taiwan, ROC; **Stress and Young's Modulus Properties of Some Metallic Thin Films**

J.-D. Kamminga; Netherlands Institute for Metals Research, Rotterdamseweg 137, NL-2628 AL Delft, NETHERLANDS; **Contributions of Substrate and Film to Scratch Test Performance**

Eiji Kusano, Takeshi Deguchi, Ken Kawamata; Advanced Materials Science Research and Development Laboratory, Hakusan, JAPAN; **Control of Internal Stress of Coatings by Inductively-coupled-plasma Assisted Pulsed Magnetron Sputtering -Deposition of Low Stress and High Density Ta₂O₅ Films**

REGISTRATION INFORMATION

November 7-9, 2005: INTERNATIONAL SYMPOSIUM ON POLYMER SURFACE MODIFICATION

November 9-11, 2005: SECOND INTERNATIONAL SYMPOSIUM ON ADHESION ASPECTS OF THIN FILMS

November 12, 2005: SHORT COURSE ON ADHESION MEASUREMENT TECHNIQUES HELD IN CONJUNCTION WITH THIS SYMPOSIUM

LOCATION:

Hilton Savannah DeSoto Hotel
15 East Liberty Street
Savannah, GA 31401
Tel: Reservations (USA, Toll free): 1-800-426-8483
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Web site: (www.desotohilton.com)

REGISTRATION:

Speaker/student \$395 each; regular attendee \$595 each. A 20% discount applies if you are attending both symposia; An additional 10% discount applies if more than 1 person is participating from the same organization.

HOTEL: Please make room reservations directly with the Savannah DeSoto Hotel. A block of rooms has been set aside for conference registrants until October 7, 2005. After this date the hotel will accept reservations on a space available basis and they cannot guarantee that the special conference rates of \$119 single/double per day will apply. Make your reservations early and be sure to mention that you are attending one of the MST symposia in order to receive the reduced conference hotel rate.

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SHORT COURSE ON ADHESION MEASUREMENT TECHNIQUES, MAY 20, 2000:

Associated with each of the above symposia MST gives a short course on adhesion measurement methods. Since nearly all of the symposia have some relation to adhesion phenomena, the ability to quantify the adhesion of one material layer to another is clearly one of the unifying themes. This course is designed to mesh with the topical symposia by presenting an overview of the most useful adhesion measurement techniques which are being used to evaluate the **PRACTICAL ADHESION** of coatings. Emphasis will be given to methods which can be carried out in a manufacturing environment as well as in the lab and which give results that are directly relevant to the durability and performance of the coatings. The effects of material elastic properties and residual stress are considered as well as other external influences which affect coating adhesion.

Audience: Scientists and professional staff in R&D, manufacturing, processing, quality control/reliability involved with adhesion aspects of coatings or laminate structures.

Level: Technical overview

Prerequisites: General background in chemistry, physics or materials science.

Duration: 1 day

Registration fee: \$495: Includes complete set of lecture notes.

How You Will Benefit From This Course:

- ▶ Understand advantages and disadvantages of a range of adhesion measurement techniques.
- ▶ Gain insight into mechanics of adhesion testing and the role of sample intrinsic stress and material properties
- ▶ Learn optimal methods for setting adhesion strength requirements for coating applications.
- ▶ Learn how to select the best measurement technique for a given application.
- ▶ Gain perspective from detailed discussion of actual case studies of product manufacturing and development problems.

CANCELLATIONS: Registration fees are refundable, subject to a 15% service charge, if cancellation is made by **October 7, 2005**. **NO** refunds will be given after that date. All cancellations must be in writing. Substitutions from the same organization may be made at any time without penalty. MST Conferences reserves the right to cancel either of the symposia or the short course if it deems this necessary and will, in such event, make a full refund of the registration fee. No liability is assumed by MST Conferences for changes in program content.

REGISTRATION FORM

POLYIMIDES AND OTHER HIGH TEMPERATURE POLYMERS November 7-9, 2005 (speaker/student)	\$395
POLYIMIDES AND OTHER HIGH TEMPERATURE POLYMERS November 7-9, 2005 (regular attendee)	\$595
ADHESION ASPECTS OF THIN FILMS, November 9-11 2005 (speaker/student)	\$395
ADHESION ASPECTS OF THIN FILMS, November 9-11 2005 (regular attendee)	\$595
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Deduct 20% if also attending both symposia. Deduct additional 10% if more than 1 participant from same institution	
Short Course on Applied Adhesion Measurement Methods: October 7, 2005	\$495
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ADDRESS:	
E-mail:	
PHONE:	FAX: