The Polyimide Story

▮ Here is a (slightly edited) article about the development of polyimides, which appeared in 2005 in the MATERIALS SCIENCE AND TECHNOLOGY NEWSLETTER.

   ● It is one of the rare articles that also mentions what went wrong. It gives a good idea how difficult it is in the real world out there to introduce a new matetial in a complex product.

   ● Here is the link to the Journal;

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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 elevated 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® (The basic resin goes under the name pyromellitic dianhydride oxydianaline or PMDA-ODA for short) film material produced 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

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seemed there would be no free lunch. If you wanted the high performance 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-methy-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 SiO_2 which is the purest form of glass known and forms the basis of nearly all glass artifacts. The glassware in your cupboard is basically SiO_2 doped with boron and other materials which are used to give the final artifact a number of desired properties such as color, density, … etc. SiO_2 was also a natural for the microelectronics industry since nearly every silicon wafer comes with a thin layer of SiO_2 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 SiO_2 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 in integrated circuits.

Amorphous SiO_2 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 SiO_2 were the problems 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 SiO_2 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 SiO_2 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 after coating.

Enter the polyimide materials. Since these materials go down as a viscous liquid, they tend to planarize the underlying topology much better than SiO_2. The degree of planarization is not perfect but is nonetheless much much better than what one gets with SiO_2. Thus it looked as though the polyimides were a natural to replace SiO_2 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 SiO_2 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 with 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" ("Structures or why Things Don't Fall Down", J. E. Gordon (Da Capo, Press, 1978) p. 63). 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 comonly 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' 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 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 ones 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? (Answer: The tendency of coatings yo 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:

$$s = E \times a \times DT/(1-v)$$

In this equation E is the modulus of the polyimide, thermal expansion difference between the polyimide and the ceramic, T the temperature excursion and Poisson's ratio of the polyimide. In this example E = 3GPa, = 1/3, a = 30×10^{-6}/C and DT = 380 C. Inserting these values into our little formula gives an expected biaxial stress of = 0.051 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 know 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. (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 <u>Surface and Colloid Science in Computer Technology</u>, Ed. K. L. Mittal (Plenum Press, New York, 1987) p.179) 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, 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.

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 SiO_2 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 electodeposited 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 is 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.