# Diffusion and self-gettering of ion-implanted copper in polyimide

J. H. Das and J. E. Morris
*Institute for Research in Electronics Packaging, Department of Electrical Engineering, T. J. Watson School of Engineering, Applied Science and Technology, State University of New York, Binghamton, New York 13901*

(Received 22 May 1989; accepted for publication 1 September 1989)

The diffusion of ion-implanted Cu in Kapton films has been studied by Rutherford backscattering. At low temperatures, diffusion is thermally activated with an energy of 0.41 eV and a diffusion constant $D$ of about $10^{-18}$ $cm^2/s$ at room temperature. Above 460 K the implanted profiles narrow dramatically instead of continuing to spread, a process interpreted in terms of cluster nucleation at the polymer's $\beta'$ transition temperature. Subsequent diffusion of the clusters above 525 K has an activation energy of 1.91 eV. The ion implantation causes discernible surface damage to the polyimide.

## I. INTRODUCTION

Polyimides form a class of organic polymers first noted for their thermal stability, resistance to irradiation, to mechanical deformation at high temperature, and to solvent attack.[1,2]

These polyimides are finding increasing use in integrated circuits, both as insulators and protective layers. Similar roles are played in the electronics packaging field, where the polyimide is also often the substrate or mechanical support for conductive (metal) thin films. Their high electrical resistivity, thermal stability, chemical inertness, superior adhesive properties to common substrates, ease of application and removal, and their ability to build up layers of various thicknesses permits their incorporation in many very large-scale integration (VLSI) processes. Polyimides can usually offer coatings of less stress than their inorganic counterparts and in many instances offer cost advantages too.[3–5]

One of the most critical aspects of VLSI and printed circuit board (PCB) applications is the interaction between the metal interconnects and polyimide insulators. Should the polyimide become sufficiently doped by the diffusion of metal atoms, so that its resistivity falls, the polyimide would lose its effectiveness as an insulator. However, controlled doping might find uses in new device design, and the feasibility of ion implantation as a means of preparing a conductive surface on polymer films is being investigated.[6] It has also been demonstrated that high doses ($10^{14}$–$10^{17}/cm^2$) of high-energy reactive ion species can lead to useful changes in polyimide properties, such as the increase of conductivity, possibly via a doping mechanism.

Such interactions between metal and polyimide are relatively poorly documented. Shanker and MacDonald[7] have addressed the issue by depositing metal films on both Pyralin 2540 and Kapton H,[8] which were thermally treated for 0.25–4 h in vacuum, nitrogen, and air over the temperature range of 375–648 K. The purpose was to measure diffusion constants for penetration of the polyimide by the metal atoms. They observed that all the Cu films heated in air or nitrogen at temperatures exceeding 518 K picked up about 55% oxygen very rapidly, suggesting a stable compound/oxide formation. The contribution of the oxide in the diffusion process was not clear.

This current work is directed towards a detailed study of the behavior of ion-implanted copper in various types of (25-$\mu$m) Kapton films. The implanted films were thermally treated for 1–7 days in air over the temperature range of 300–623 K. The purpose of the study is to extend the work of Shanker and MacDonald[7] in the study of the diffusion of the copper implant profile inside the film, remote from surface effects, possibly providing additional information on the rôle of the oxide (or oxygen). In addition, the data may be applicable to the thermal stability of an ion-implanted conductive surface. Diffusion effects were monitored by RBS (Rutherford backscattering spectroscopy).

## II. THEORY

The implant profile of copper can be approximated as Gaussian. When the initial distribution is Gaussian with a peak concentration $N_p(t)$ at $R_p$ and a half-width $W(t)$, the solution to the diffusion equation is particularly simple, provided that the diffusion constant $D$ is concentration independent.[9] The concentration $N(x,t)$ at a depth $x$ after a diffusion time $t$ is expressed as

$$N(x,t) = N_p(t)\exp-\left(\frac{(R_p - x)^2}{2W(t)^2}\right), \tag{1}$$

where

$$N_p(t) = 0.399Q/W(t), \tag{2}$$

$Q$ is the total concentration, and $W(t)$ is given by

$$W(t)^2 = W(0)^2 + 2Dt. \tag{3}$$

Equation (1) is simply a Gaussian centered at $R_p$ (independent of $t$) with a variance given by Eq. (3). Equations (1)–(3) are valid as long as time is short enough to ignore the boundary conditions so that $4Dt$ is much less than $R_p^2$, i.e., the diffusing profile edge will not reach the polyimide surface. If these conditions are met, knowledge of the distribution at two times $t_1$ and $t_2$ is sufficient to allow a reliable calculation of the diffusion constant $D$ from $W(t)$, found either directly or from $N_p(t)$. In this study the ion-implanted Cu profile was approximated as a Gaussian profile at time $t_1$, and the profile at later $t_2$ was obtained for selected temperatures.

 © 1989 American Institute of Physics 

## III. EXPERIMENT

Copper was ion implanted into H, HN, V, and VN Kapton types. All four types possess the same chemical compositions[10]; type H is the older version of HN, and V is the older version of VN. Type V and VN are dimensionally stabilized by the manufacturer.

These films were implanted with 1–5 $\times 10^{16}$ $cm^{-2}$ 225-keV $Cu^{4+}$ ions at room temperature at Cornell University's National Nanofabrication Center. The implant current was restricted by the capacity of the implanter, the maximum current obtainable being in the microampere range. Each implant time extended from 30 to 60 min. Implanted areas of the film were visibly darker than the rest, indicative of surface damage.

These films were subsequently thermally treated for varying times (1–7 days) in the temperature range of 300–623 K ($\pm 5$ K). At temperatures exceeding 453 K, the films regained some of their original color (i.e., texture), indicating annealing or smoothing of the surface, or (as will be argued below) loss of the damaged surface layer. In this temperature range some films also exhibited a bright golden color momentarily as they were withdrawn from the oven, indicating traces of Cu at the surface of the film, before turning dark.

RBS data were taken using a 2.2-MeV $He^{2+}$ beam, also at Cornell University. The raster scanned beam current was restricted to $< 20$ $nA/cm^2$. Depending upon the intensity of the Cu spectrum, the current integration ranged between 5 and 12 $\mu C$. Such a low current was used to minimize beam damage, and the relatively low energy of 2.2 MeV was used for a better resolution of the spectrum. The area of the film exposed to the beam appeared darker than the rest, indicating again that some beam damage did occur.

No microscopic surface analysis was done, and so it was not possible to measure the extent of the surface damage directly.

## IV. RESULTS

### A. Diffusion and self-gettering of copper

One sample RBS spectrum is shown in Fig. 1. The C, N, and O counts of the substrate overlap each other in the lower energies, while the implanted Cu shows up as the high-energy Gaussian. The RBS data was matched to the expected Gaussian profiles by methods outlined elsewhere.[11–14]

For a typical implanted Cu profile, $R_p$ and $W(0)$ were found to be 320 and 140 nm, respectively. The conversion from the intrinsic RBS depth unit of $atoms/cm^2$ assumes a constant uniform polyimide density equal to the manufacturer's published value, with negligibly dilute implants. The nominal compositions of all types of films prior to implantation were found to be the same with $C = 57.9\%$, $H = 26.3\%$, $N = 5.2\%$, and $O = 10.5\%$.[15]

The effects of thermal treatments can be classified into three groups over distinct temperature intervals.

(a) At temperatures below 460 K, the activation energy of diffusion is about 0.41 eV and the diffusion constant ranges from $10^{-18}$ to $10^{-15}$ $cm^2/s$ as shown in Fig. 2. The effect of temperature on metal diffusion in this region is visually evident from a comparison of profiles 1 and 2 in Fig. 3. Profile 1 is as-implanted, and profile 2 follows heating in air for 48 h at 453 K. There is a broadening of the profile with the expected decrease in the peak height of Cu. Below 460 K, all profiles behave in this expected fashion.

(b) In the temperature range from 460 to about 525 K, self-gettering of the Cu has been observed, as shown by the narrowing of profile 3 in Fig. 3. In some cases peak concentration was found to be as high as four times the initially implanted peak value with an appropriate reduction in $W$.

(c) In the temperature range between 525 and 623 K, further diffusion was observed with the much higher activation energy of about 1.91 eV. Profile 4 of Fig. 3 shows a

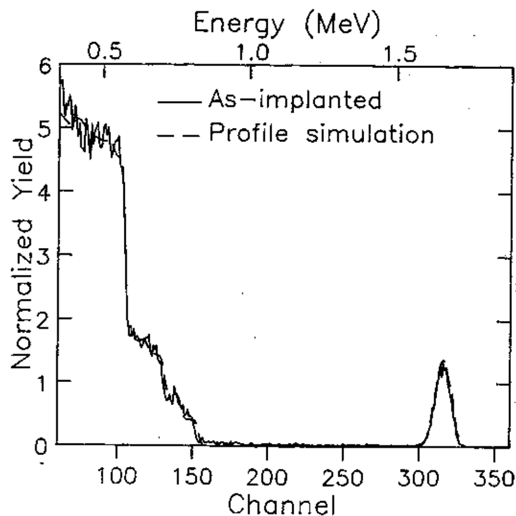


FIG. 1. As-implanted RBS spectrum of Cu in H-type Kapton, with profile simulation.

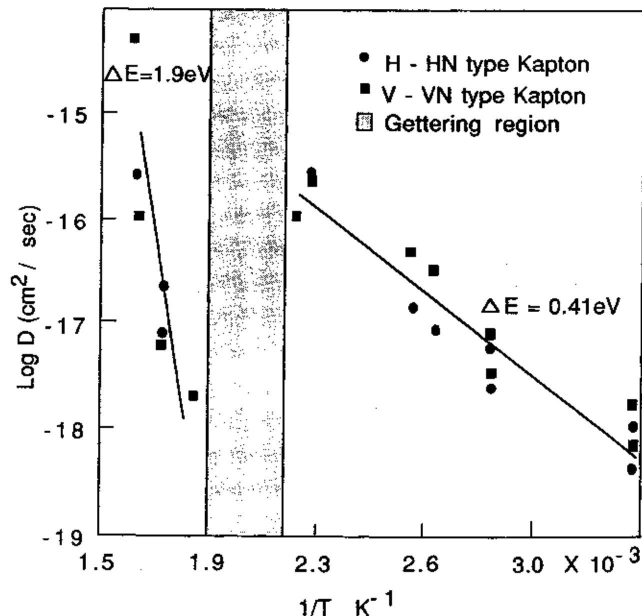


FIG. 2. The variation of the diffusion coefficient of Cu in polyimide with inverse temperature.

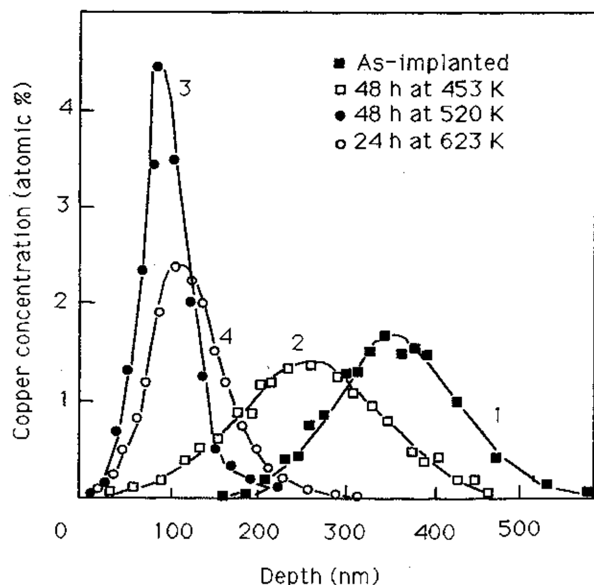


FIG. 3. Concentration of Cu in VN-type Kapton as a function of depth and thermal treatment.

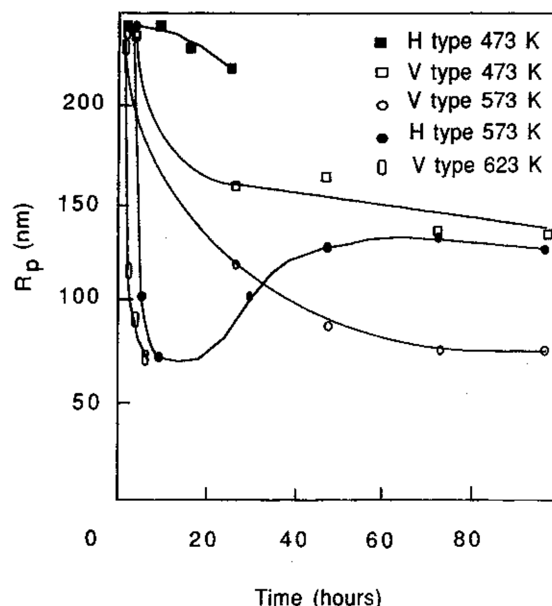


FIG. 4. Profile peak position as a function of time and temperature.

typical distribution at 623 K, with a higher $W$ and a lower peak than profile 3. If the self-gettering process above leads to nucleation of Cu islands within the polyimide, then the 1.91 eV may well correspond to the cluster diffusion.

### B. Thermal stability of polyimide films

From Fig. 3, profiles 1, 2, and 3, a shift of the Cu profile towards the surface is noted with the increase in temperature. Since no convincing mechanism has been determined for such movement of the whole implant, it is believed that the result indicates loss of surface material instead. In Fig. 4, the peak positions of various samples are shown to move more rapidly towards the surface as the temperature is raised, which is consistent with this interpretation.

In one case in Fig. 4, it is noted that $R_p$ appears to drift back into the film interior, and a similar effect is seen comparing profiles 3 and 4 of Fig. 3. This is tentatively attributed to eventual distortion of the ideal Gaussian as reflection of diffusing ions from the polymer surface back into the interior begins to develop some significance.

RBS data (Fig. 5) also shows a relatively low surface concentration of constituent O in the as-implanted films, which is attributed to surface damage. The concentration gradation vanishes after annealing, consistent with the loss of the surface layer.

Finally, Fig. 6 shows the average relative concentration of oxygen in the film across a 100-nm layer at a depth of 150 nm. Following the argument above, the effective sample region is assumed to move deeper into the polyimide film as the temperature is raised and surface material is lost. The initial low O content (at about 50% of the manufacturer's nominal expected value) corresponds to the oxygen depleted surface layer. Up to 373 K, the damaged surface layer appears to be fairly stable. Heating times of 7 days were used in this temperature range.

A sharp rise in O content is noted over the temperature range of 433–453 K where 2-day heating periods were used. It is assumed that the surface layer is lost within this temperature range, but note that the O content exceeds the expected value for bulk Kapton. It appears that there is some additional oxidation effect here.

Beyond 530 K, O content falls sharply as the film decomposes. Organic molecules typically oxidize between 523 and 623 K in air,[16] and the O loss at observed temperatures is consistent with DuPont data.[17,18]

Note that RBS provides no information on H content. In Fig. 5, the N content also appears to be reduced at the surface, but the effect is obscured by the O level. In surface carbonization, all three constituents would be depleted.[19]

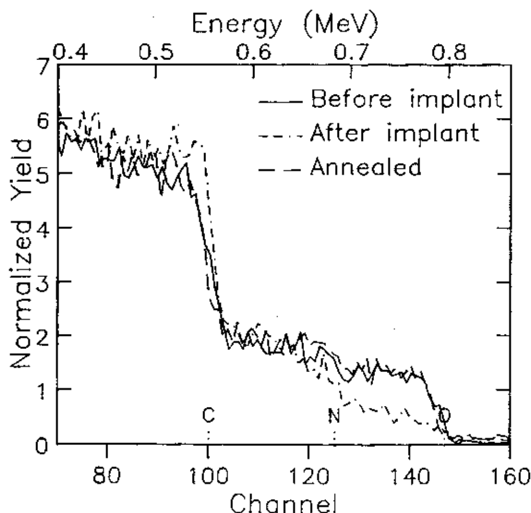


FIG. 5. RBS profiles showing the effects of oxygen depletion after implant. (The C, N, and O edges are indicated; 24-h annealing at 623 K.)

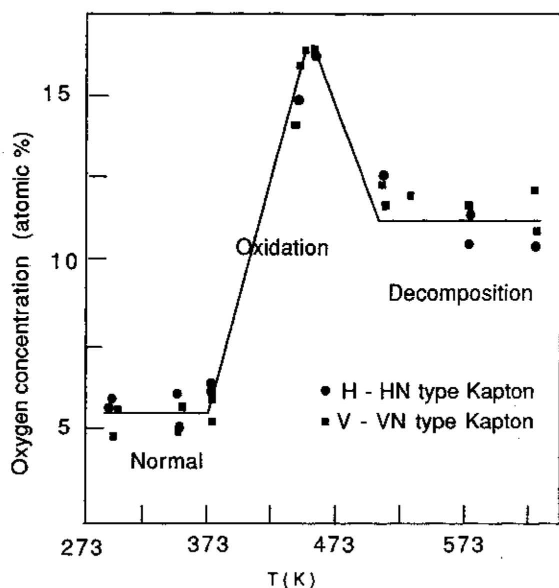


FIG. 6. Concentration of oxygen in polyimide as a function of temperature, demonstrating the oxidation peak prior to the onset of decomposition.

## V. DISCUSSION

During this work, the polyimide films were exposed to two types of high-energy beam irradiations: 225-keV $Cu^{4+}$ during implant action and 2.2-MeV $He^{2+}$ for RBS analysis. Polyimides either cross link or degrade under beam irradiation. The behavior of materials under ion beams depends on the experimental conditions, and damage must be minimized by an adequate choice of instrumental parameters. Ion-beam techniques have been used in the past for the study of diffusion in polymers and results were found to be satisfactory.[7,20-22] Irradiation damage of polyimide by $He^{2+}$ ions under very similar experimental conditions to the RBS work here has been reported to be negligible.[23] But irradiation during the Cu implant process appears to produce considerable damage to the surface. During thermal treatment, stripping of this disordered region accounts for the apparent movement of the implant distribution towards the surface.

From the constant source diffusion study,[7] it was also reported that Cu films heated in vacuum exhibited little change in $D$ with temperature ($10^{-15}$ $cm^2/s$ from 516 to 623 K), whereas there is a marked temperature variation of Cu diffusion in the presence of air. Cu was reported to oxidize inside polyimide films heated in air.[24] Although Cu is expected to behave differently inside the film than at the interface, the effect of these oxides on diffusion is not clear and needs further investigation.

The low-temperature diffusion results are in fair agreement with the results obtained from a constant source diffusion,[7] i.e., from a deposited surface film of Cu. In the constant source diffusion, the activation energy was about 0.65 eV over the complete temperature range of 375–648 K, compared to the 0.41 eV measured here. At 433 K the $D$ value was in the $10^{-15}$-$cm^2/s$ range in both cases. At this temperature it would take approximately 4 months for diffusing copper atoms to pass through a 1-$\mu$m Kapton film. In past ion implant studies with 3-MeV $Cu^{4+}$,[6] some changes in electrical and chemical properties of polyimide were found, including the formation of complexes, but the implant energy in the work here was only a fraction of that. The effects of complex formation here, if any, appear to be negligible from the similarities in activation energies determined for diffusion from the deposited and implanted sources.

The high-temperature diffusion coefficient drops dramatically above the aggregation temperature range. As suggested earlier, the higher activation energy may be associated with the diffusion of the islands.

Though gettering is a well-known process,[25,26] it has never been explicitly observed in the Cu-polyimide system before. The mechanism responsible for self-gettering cannot be defined yet, although one can indulge in some speculations.

In a study of gettering of Cu in ion-beam-damaged regions in gallium phosphide and gallium arsenide,[26] Cu was found to accumulate at the interface between the amorphous region and the undamaged crystal; the gettering process was related to the annealing of implantation damage. One might draw an analogy between these two processes. In polyimide, Cu gettering appears to be a thermally activated process, and if the shift of the position of the implant peak is considered to be due to the loss of the surface material, the peak location can obviously be expected to lie at the interface between the undamaged film and the damaged surface region.

Polyimide-Cu interfaces have been under investigation for quite some time. It was reported that Cu deposited on polymer results in island or cluster formation at the surface due to a weak interfacial interaction.[27] Recently, the formation of subsurface particles was reported, when some elements, including Cu, were vacuum deposited on to soft polymer substrates.[28-31] In this process a particle sinks completely into the substrate if the work of adhesion of the particle material to the substrate material is greater than the work of cohesion of the substrate material, i.e., if the substrate molecules prefer to interact with the particle molecules rather than themselves.[30] It is a fundamental concept in nucleation theory that the embryonic Cu cluster immersed in the host phase will form and be stable only if its total free energy is less than that of the host phase. The total free-energy change[32] is due to a change in the (negative) bulk free energy which decreases as radius ($r^3$) and a (positive) surface free energy which increases as radius ($r^2$). The onset of self-gettering and cluster nucleation over a specific temperature range is provisionally attributed to a change in the bulk free energy of the polymer at that temperature. To validate the concept of a bulk free-energy change, one must seek a plausible phase change at the appropriate temperature range. The obvious choice is the glass transition temperature $T_g$ (where several physical parameters change), but at 633 K, typically, $T_g$ is clearly too high, unless it is somehow lowered by surface damage. The 473–533-K range does, however, coincide with the temperature range of the second order $\beta'$ relaxation process. (There are typically several distinct dielectric relaxation processes present in a solid polymer. As the temperature is raised, molecular mobilities of various types become available for dipolar orientation.[33-36]

These same relaxation processes are also generally responsible for dispersions in mechanical properties.[37] In a second-order process, the thermal derivative of the physical parameter exhibits a discontinuity, whereas in a first-order process it is the parameter itself which does so. The $\beta'$ process, which is amplified by residual solvent in the polymer, is a prominent example of the second-order type. It is noted in passing that the assumed glass transition in Kapton also shows empirical second-order characteristics rather than the first order expected.)

These factors mentioned above might be responsible singly or in combination for the gettering process which needs to be further investigated. But it does appear that there is a correlation between the second-order $\beta'$ phase transition, the absorption of oxygen by the polyimide, and possible changes in the bulk or Cu-interfacial energies of the polyimide (during Cu nucleation) since all appear over roughly the same temperature range.

## VI. CONCLUSION

No significant differences were observed in the results for the four different Kapton types used. There is evidence of surface roughening and carbonization of the polyimide surface during Cu implantation.

Low-temperature diffusion results were in fair agreement with the constant source diffusion data, whereas the high-temperature diffusion coefficient was found to be much lower, suggesting the possibility of the diffusion of Cu islands instead of Cu atoms. Cu cluster formation in polyimides has been observed before, but the identification of the limited temperature range over which it occurs is new. Although the mechanism responsible for self-gettering was not determined, it is tentatively attributed to a change in bulk energy of the polyimide at the $\beta'$ transition.

This work is continuing with similar studies of other metals and polymers. A study of polyimide bulk energy through the $\beta'$ phase transition may also be profitable.

## ACKNOWLEDGMENTS

This work would not have been possible without the support of R. Horwath and F. Emmi of IBM (Systems Technology Division) at Endicott, NY. The ion implantations were performed by M. Skvarla of the National Nanofabrication Center at Cornell University. RBS studies were also performed at Cornell in the Department of Materials Science with the permission of J. Mayer.


[1] C. E. Sroog, A. L. Endrey, S. V. Abramo, C. E. Berr, W. M. Edwards, and K. L. Oliver, J. Polym. Sci. A **3**, 1373 (1965).

[2] J. Duran and N. S. Viswanathan, ACS Symp. Ser. **242**, 239 (1984).

[3] D. D. Denton, D. R. Day, D. F. Priore, and S. D. Senturia, J. Electron. Mater. **14**, 119 (1985).

[4] T. Dietz, J. N. Zemel, I. Lauks, and T. Carrol, Thin Solid Films **119**, 439 (1984).

[5] F. W. Smith, H. J. Neuhaus, S. D. Senturia, Z. Feit, D. R. Day, and T. J. Lewis, J. Electron. Mater. **16**, 93 (1987).

[6] M. P. Zussman, S. Wood, L. C. Scala, J. Bartko, and A. Vincentz, J. Appl. Polym. Sci. **35**, 2183 (1988).

[7] K. Shanker and J. R. MacDonald, J. Vac. Sci. Technol. A **5**, 2894 (1987).

[8] Registered trademark of DuPont Co., Wilmington, DE.

[9] B. L. Crowder, J. F. Ziegler, F. F. Morehead, and G. W. Cole, *Ion Implantation in Semiconductors and Other Materials (Proceedings)* (Plenum, New York, 1973), pp. 267–274.

[10] *Kapton Polyimide Film: Summary of Properties* (DuPont Co., Wilmington, DE).

[11] W. K. Chu, J. W. Mayer, and M. A. Nicolet, *Backscattering Spectrometry* (Academic, New York, 1978).

[12] L. R. Doolittle, Nucl. Instrum. Methods B **9**, 344 (1985).

[13] L. R. Doolittle, Nucl. Instrum. Methods B **15**, 227 (1986).

[14] L. R. Doolittle, *RUMP Users Guide* (Cornell University, Ithaca, NY, 1985).

[15] F. Foroughi, B. Vuilleumier, and E. Bovet, Nucl. Instrum. Methods **159**, 513 (1979).

[16] P. E. Cassidy, *Thermally Stable Polymers* (Dekker, New York, 1980), pp. 5–28.

[17] *Kapton Decomposition Products Technical Information* (DuPont Co., Wilmington, DE).

[18] Private communication, Electronics Dept., DuPont Co., Wilmington, DE.

[19] S. Contarini, J. A. Schultz, S. Tachi, S. Y. Jo, and J. W. Rabalais, Appl. Surf. Sci. **28**, 291 (1987).

[20] M. A. Selen and J. R. Macdonald, Nucl. Instrum. Methods **218**, 451 (1983).

[21] R. C. Lasky, E. J. Kramer, and C.-Y. Hui, Polymer **29**, 673 (1988).

[22] R. C. Lasky, E. J. Kramer, and C.-Y. Hui, Polymer **29**, 1131 (1988).

[23] L. J. Matienzo, F. Emmi, D. C. Van Hart, and T. P. Gall, J. Vac. Sci. Technol. A **7**, 1784 (1989).

[24] S. A. Ezzell, T. A. Furtsch, E. Khor, and L. T. Taylor, J. Polym. Sci. **21**, 865 (1983).

[25] H. Kerkow and G. Kreysch, Wiss. Z. Humboldt-Univ. Berlin, Math.-Naturwiss. Reihe **31**, 361 (1982).

[26] W. Frentrup, M. Griepentrog, H. Klose, and U. Muller-Jahreis, Extended Abstract, 16th Conference on Solid State Device Mater., 1984, pp. 301–304.

[27] R. C. White, R. Haight, B. D. Silverman, and P. S. Ho, Appl. Phys. Lett. **51**, 481 (1987).

[28] M. Pattabi, M. S. Murali Sastry, and V. Sivaramakrishnan, J. Appl. Phys. **64**, 437 (1988).

[29] G. J. Kovacs and P. S. Vincett, J. Colloid. Interface Sci. **90**, 335 (1982).

[30] G. J. Kovacs, P. S. Vincett, C. Tremblay, and A. L. Pundsack, Thin Solid Films **101**, 21 (1983).

[31] G. J. Kovacs and P. S. Vincett, Thin Solid Films **100**, 341 (1983).

[32] B. L. Davis, Nucleation Processes in Cloud Physics, Lecture notes, S. D. School of Mines & Technology, Rapid City, 1976, pp. 59–74.

[33] W. Wrasidlo, J. Polym. Sci. A **9**, 1603 (1971).

[34] W. J. Wrasidlo, J. Polymer. Sci. Polym. Phys. Ed. **11**, 2143 (1973).

[35] R. M. Ikeda, Polym. Lett. 4, 353 (1966).

[36] A. R. Blythe, *Electrical Properties of Polymers* (Cambridge University, Cambridge, UK, 1979), pp. 46–59.

[37] S. Isoda, M. Kochi, and H. Kambe, J. Polymer Sci. Polym. Phys. Ed. **20**, 837 (1982).