Open access • Journal Article • DOI:10.1063/1.353824

Composite conduction in ion-implanted polymers — Source link

Yongqiang Wang, L.B. Bridwell, Ryan E. Giedd

Published on: 01 Jan 1993 - Journal of Applied Physics (American Institute of Physics)

Topics: Ion track, Conductivity and Variable-range hopping

12-1-1993

Composite conduction in ion-implanted polymers

Yong-Qiang Wang
MSU Graduate Student

L. B. Bridwell
Missouri State University

Ryan E. Giedd
Missouri State University

Recommended Citation

Wang, Yongqiang, L. B. Bridwell, and R. E. Giedd. "Composite conduction in ion-implanted polymers." Journal of applied physics 73, no. 1 (1993): 474-476.

Composite conduction in ion-implanted polymers

Yongqiang Wang,[a] L. B. Bridwell, and R. E. Giedd
Department of Physics and Astronomy, Southwest Missouri State University, Springfield, Missouri 65804

(Received 17 March 1992; accepted for publication 18 September 1992)

The temperature dependence of the dc conductivity for polyamide-imide films, implanted with 50 keV As ions to different fluences, has been studied. Our high-resolution data reveal a two-component conductivity that depends on both one-dimensional variable range hopping (VRH) and three-dimensional VRH. For low fluence levels (5×10^{15} ions/cm^2), the one-dimensional VRH is dominant while at higher fluences (1×10^{17} ions/cm^2), the three-dimensional VRH dominates. These materials become highly disordered and form hard carbon materials along the ion track. The conductivity may be explained by 1D VRH along the ion track at low fluences while at higher fluences, regions of carbon rich material form three-dimensional structures where 3D VRH exists. This rather simple model and its composite conductivity can explain the exact curvature of the temperature dependent conductivity, while single VRH models and percolation models cannot.

Enhancing the electrical properties of polymers is an important area of technology since polymers are so widely used. Possible applications range from antistatic coatings to polymer field effect transistors.[1]

One method of changing an insulating polymer into a conducting material is by ion implantation or plasma etching. In the case of ion implantation, damage to the bulk of the material in the form of dangling bonds, polymer scission, emission of volatile molecules, and additional cross linking occurs, while in the plasma etching technique, damage occurs only at the surface. The effects of ion implantation have been studied as a function of energy, ion species, polymer species, ion beam current, and implant fluence.[2] Surprisingly, the differences in ion species and polymer species are significantly reflected in the final electrical conductivity of the material.[3,4] This is especially true at lower energies. At higher energies, very hard carbon materials have been seen to occur.[5,6]

There are a number of studies on the conductivity of ion-implanted polymers.[3–5,7–11] In spite of this large amount of data, a definitive model that fits the conductivity over a large temperature range seems elusive. The work presented here is for relatively low-energy implants, about 50 keV, at higher fluences (over 1×10^{17} ions/cm^2). These materials form much differently than materials implanted with higher energy ions. High-energy implants form much harder carbon materials in the vicinity of the ion track.

The physical structure of an implanted polymer has been studied for the low fluence case, and is not easily extrapolated to higher fluences. A qualitative picture of the structure is that of "tree-like" ion tracks that branch more often as the ion approaches its mean range.[10] The material at the surface has a different type of damage than does the material beneath the surface. This is a result of the differences in the way the ion couples to the structure as it loses energy. There tends to be wider, larger regions of damage toward the end of the ion track, a result of the increased efficiency in ion coupling to the polymer lattice as the ion loses energy. The creation of secondary particles also tends to do the most damage in this region. It is possible to contain the ion damaged material within a "teardrop"-shaped geometry.

At higher fluences these teardrop structures should overlap, resulting in a percolation-type dependence in the conductivity. There are a number of reasons why this might not occur. First, it is uncertain that the conductivity of the damaged region is orders of magnitude better than the undamaged region, making the transition at the percolation threshold small. Second, considerable tunneling may occur before the structures actually overlap, further obscuring the threshold. The percolation threshold may be more obvious in higher energy implants since the conductivity of the damaged carbon material is larger.

Therefore, the problem reduces to the study of the dominant conduction mechanism in the damaged, teardrop regions, which is probably different for different regions within the teardrop. Among the models studied for this process are one-dimensional variable range hopping (VRH),[12] three-dimensional VRH,[13] and the charged-energy-limited tunneling model.[14] One-dimensional VRH has been given the most attention in previous work,[3,7,8,10] however, the charged-energy-limited tunneling model is also used quite extensively.[4,11]

In our experiments, the temperature-dependent conductivities of six polyamide-imide samples, synthesized in our laboratory and implanted with 50 keV As ions to varying fluences, were measured. The resistance of the samples were measured by Keithley instrumentation, using a constant voltage method, in the temperature range 70–300 K. The macroscopic homogeneity as measured by optical microscopy was verified to be better than 5%. The data have accuracies of about ±1% in surface resistance below 5×10^9 Ω and about ±2% in temperature above 70 K. Low electric fields were used as a result of keeping the evaporated gold or nickel electrodes 2.5 cm wide and 0.7 cm apart. The relative precision of the data is better, 9.6

---

[a] Permanent address: Department of Modern Physics, Lanzhou University, Lanzhou, People's Republic of China.

0021-8979/93/010474-03$06.00

$\times 10^{-6}$ for the resistance domain and for the temperature domain, 4.4×10^{-4}.

The one-dimensional VRH and charged energy limited tunneling models predict identical expressions for the dc electrical conductivity. This dependence is of the form

$$\sigma_1(T)\exp[-(T_1/T)^{1/2}],$$

where the prefactor $\sigma_1(T)$ is a slowly varying $1/T$ dependence that is dominated by the exponential dependence. The prefactor has been included in some work[15] and treated as a constant by others.[3,7,8,10] We tried fitting the data both ways and found them equivalent within experimental error. It is, however, essential to include the $1/T$ dependence when determining the physical significance of the prefactor. In terms of general behavior, the above expression did not fit our data over any large temperature interval, especially for the high-fluence implanted samples (e.g., 1×10^{17} ions/cm^2). We were only successful in fitting the above equation to our data when the temperature region was small enough so that the differences in curvature between our data and the above expression were within experimental error.

A similar result was obtained for three-dimensional VRH, where the expression for the conductivity as a function of temperature is

$$\sigma_3(T)\exp[-(T_3/T)^{1/4}],$$

where $\sigma_3(T)$ is a slowly varying $1/T^{1/2}$ dependence relative to the exponential term. As with the case of one-dimensional VRH, this expression would not fit our data over any large temperature regime, especially for the low-fluence implanted samples (e.g., 5×10^{15} ions/cm^2).

The one-dimensional VRH model and the three-dimensional VRH model represent applications of the general VRH formalism to structures of varying dimensionality. Considering the physical structure of the ion track in the material and assuming that this ion track provides carriers for the conduction process, might lead to a conclusion that the dimensionality of the material may be somewhere between three and one. Indeed it has been speculated previously that the ion tracks have a fractal geometry.[10] Based on these assumptions, we fit the data the form

$$\sigma_n(T)\exp[-(T_n/T)^{1/n+1}],$$

so that we had a variable dimensionality, n. The fit that was performed was necessarily nonlinear; however, the small number of parameters made the program converge quickly and apparently uniquely. This model yielded unsatisfactory results. The value of n was not constant as a function of fluence. The nonintegral values of the n obtained from this fitting is hard to explain in terms of dimensionality. In some cases, n was even greater than three or smaller than 1. Although the fractal concept[16] has been used to describe the geometrical structure of polymers and the density of the states for thermal vibrations in polymers, there is no apparent reason to surmise that the electrical conduction process in polymers results from excitations in fraction-dimensional space instead of the Euclidean space. More importantly, there remained a difference in curvature between the fitted results of this general formula and the experimental data.

TABLE I. Comparison of the reduced χ_ν^2's obtained from different conduction models for ion-implanted polymers.

Ion fluence (ions/cm^2)	Conduction models		
	1D VRH	3D VRH	Composite
5×10^{15}	90.24	743.34	12.35
1×10^{16}	105.85	379.50	12.88
2×10^{16}	178.14	222.06	1.95
5×10^{16}	296.62	121.22	6.77
1×10^{17}	479.05	78.45	0.64
2×10^{17}	1048.93	47.61	1.84

Another possibility was that the assumption (that there exists a singular conduction mechanism in the material) is incorrect. It is possible that conduction along the ion tracks is of a much different nature than the conduction within the highly disordered region toward the bottom of the teardrop. We speculated that the conduction along the ion track would be one-dimensional in nature because the track itself is one dimensional. Conduction in the highly disordered region, toward the mean range of the ion, may be three dimensional because of the large number of dangling bonds and polymer fragments present in this region. These assumptions would yield a composite conductivity of the form

$$\begin{aligned}\sigma(T)&=\sigma_{1D}+\sigma_{3D}\\&=\sigma_1(T)\exp[-(T_1/T)^{1/2}]\\&\quad+\sigma_3(T)\exp[-(T_3/T)^{1/4}],\end{aligned}$$

where the conduction mechanisms contribute in a parallel manner.

The data were analyzed in terms of the composite conduction model by a Newton nonlinear least-square method. The reduced χ_ν^2's for this fit, compared with the single 1D or 3D VRH model presented above, is shown in Table I. If we assume that the prefactors $\sigma_1(T)$ and $\sigma_3(T)$ are independent of temperature. we can still get essentially same fit. Table I indicates that the only model that fit our data within experimental error is the composite conduction model. Figure 1 shows a typical fit for the composite conduction model to the experimental data for two samples. The fitting program converges quickly to values for T_1 and T_3, indicating rapid slope in the parameter space within the region of the optimum fit. The prefactors converge more slowly, indicating that the fit is less sensitive to these values. The number of significant digits in the parameters is estimated to be about 3 or 4.

The characteristic temperatures T_1 and T_3 seem to decrease with increasing fluence except for the sample with the highest fluence (2×10^{17} ions/cm^2). For example, as the fluence increases to 1×10^{17} ions/cm^2, T_1 decreases to about 22% of its value at a fluence of 5×10^{15} ions/cm^2 whereas T_3 decreases to about 2% of its value at the lower

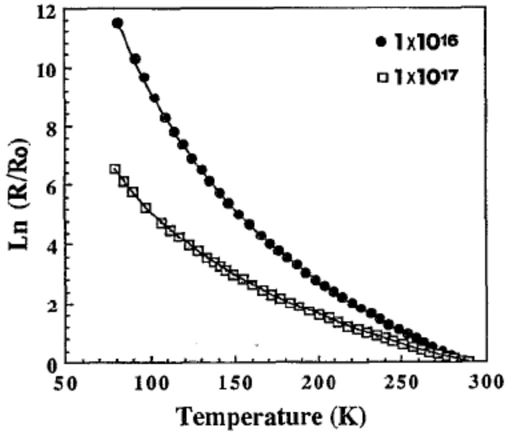

FIG. 1. Typical fitted results of surface resistance vs temperature for two ion-implanted samples.

fluence. These changes in the characteristic temperatures indicate that the 3D VRH conduction process becomes more dominant at higher fluence. This is consistent with the qualitative picture of the bottom of the treardrop region (where the 3D VRH conduction occurs) starting to overlap at higher fluence. From Mott's hopping conduction theory,[13] we can obtain the average activation energy W_3 as

$$W_3=0.6k(T^3T_3)^{1/4}$$

for 3D VRH, and the average activation energy W_1 as

$$W_1=2.0k(TT_1)^{1/2}$$

for 1D VRH. At room temperature, W_1 decreases from 0.71 to 0.34 eV, while W_3 decreases from 0.74 to 0.27 eV as the fluence increases.

Figure 2 shows the relative contribution of the 1D and 3D VRH terms as a function of temperature for the six samples. This graph demonstrates that in the temperature range of 70–300 K, both contributions to the overall conduction in the material are important. At lower temperatures, as with less disordered samples, the 1D VRH dominates. At higher temperatures and higher fluence materials, 3D VRH appears to be most important. The curvature change for the highest fluence implanted sample in Fig. 2 may be due to arsenic precipitation in the implanted layer from a "super dose" that may have influenced the conduction process.

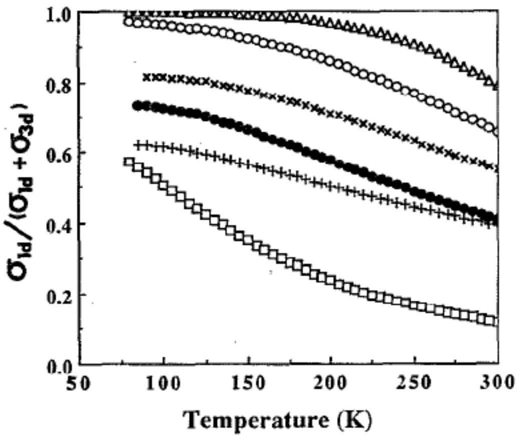

FIG. 2. Ratio of 1D VRH contribution and 3D VRH contribution vs temperature for the polymers implanted with different fluences: 5×10^{15}(△), 1×10^{16}(○), 2×10^{16}(×), 5×10^{16} (●), 1×10^{17} (+), and 2×10^{17} ions/cm^2 (□).

In conclusion, our results support the hypothesis that a temperature-dependent resistivity as predicted by phonon activated VRH is the primary method of electronic conduction in these materials. There are temperature regimes where 1D or 3D VRH dominates. However, over the large intermediate temperature range, both these mechanisms contribute to the conduction process. The combination model for conduction in these materials is not too surprising given the large amount of differing types of damage as a result of ion implantation. The nonlinear fitting process used to fit the composite conduction model to our data seems justified in this case as a result of the strong relationship between the model and the physical nature of the material.

We would like to acknowledge Dr. S. S. Mohite for supplying the polymer material, and Y. P. Feng for assisting in part of the experiments. Thanks to the undergraduate students, S. Thomas and D. Robey, for their participation in this work. Partial support for this work was provided by the National Science Foundation's Instrument and Laboratory Improvement Program through Grant No. USE-9050469.

[1] K. Yoshida and M. Iwwaki, Nucl. Instrum. Methods B **19**, 878 (1987).
[2] Y. Q. Wang, Ph.D. thesis, Lanzhou University and Southwest Missouri State University, 1991.
[3] L. B. Bridwell, R. E. Giedd, Y. Q. Wang, S. S. Mohite, T. S. Jahnke, I. M. Brown, C. J. Bedell, and C. J. Sofield, Nucl. Instrum. Methods B **56/57**, 656 (1991).
[4] Y. Q. Wang, R. E. Giedd, S. S. Mohite, T. S. Jahnke, L. B. Bridwell, and C. J. Sofield, Mater. Lett. **12**, 21 (1991).
[5] C. J. Bedell, C. J. Sofield, L. B. Bridwell, and I. M. Brown, J. Appl. Phys. **67**, 1736 (1990).
[6] E. H. Lee, M. B. Lewis, P. J. Blau, and L. K. Mansur, J. Mater. Res. **6**, 610 (1991).
[7] M. S. Dresselhaus, B. Wasserman, and G. E. Wnek, Mater. Res. Soc. Symp. Proc. **27**, 413 (1984).
[8] B. S. Elman, M. K. Thakur, D. J. Sandman, M. A. Newkirk, and E. F. Kennedy, J. Appl. Phys. **57**, 4996 (1985).
[9] T. Venkatesan, L. Calcagno, B. S. Elman, and G. Foti, in *Ion Beam Modifications of Insulators*, edited by P. Mazzoldi and G. W. Arnold (Elsevier, Amsterdam, 1987), p. 301.
[10] B. Wasserman, Phys. Rev. B **34**, 1926 (1986).
[11] S. R. Forrest, M. L. Kaplan, P. H. Schmidt, T. Venkatesan, and A. J. Lovinger, Appl. Phys. Lett. **41**, 708 (1982).
[12] W. Brenig, G. H. Dohler, and H. Heyszenau, Philos. Mag. **27**, 1093 (1973).
[13] N. F. Mott, Philos. Mag. **19**, 835 (1969).
[14] P. Sheng, B. Abeles, and Y. Arie, Phys. Rev. Lett. **31**, 44 (1973).
[15] V. K. S. Shante, C. M. Varma, and A. N. Bloch, Phys. Rev. B **8**, 4885 (1973).
[16] S. Alexander, C. Laermans, R. Orbach, and H. M. Rosenberg, Phys. Rev. B **28**, 4615 (1983).