Percolative Metal-Insulator Transition in Excimer Laser Irradiated Polyimide

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The metal-insulator transition observed in excimer laser irradiated polyimide is presented as a new experimental method to study three-dimensional percolation. The conductivity critical exponent t and the percolation threshold Φ_c are measured *in situ* for the transition under both Ohmic and non-Ohmic conditions. The experimental values obtained in the Ohmic case were $\Phi_c = 0.31 \pm 0.06$ and $t = 2.00 \pm 0.05$. These values are in close agreement with theory. The dependence of the critical exponent on current voltage characteristics of conducting sites is demonstrated for the first time.

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Percolative phase transitions are the simplest type of phase transition exhibiting nontrivial critical behavior. A metal-insulator transition can be described by continuum percolation models where conducting sites are distributed in a spatially random fashion throughout an insulating medium. When the volume fraction of conducting material, Φ, is less than a critical volume fraction Φ_c, no macroscopic conducting pathway exists and the composite remains in the insulating phase. When the volume fraction is greater than the critical volume fraction, the material becomes electrically conducting. The conductivity is described by the relation [1–3]

$$\sigma = \begin{cases} 0 & \text{for } \Phi < \Phi_c \\ \sigma_0(\Phi - \Phi_c)^t & \text{for } \Phi > \Phi_c \end{cases} \quad (1)$$

where t is the critical conductivity exponent and σ_0 is a proportionality constant. The critical exponent t is universal for a large class of lattice geometries including a three-dimensional continuum of interpenetrating spheres [4] and depends only on the dimensionality of the system and the current-voltage relation of the conducting sites. The critical volume fraction Φ_c depends strongly on the details of the lattice geometry and the shape of the conducting sites [1–4]. The experimental determination of the critical exponent t takes on particular importance since it is directly related to more fundamental parameters of percolation theory such as the correlation length exponent and the random walk fractal dimension which are difficult to determine experimentally [3]. Percolation is closely related to the theory of random resistor networks and both pictures will be used in this paper.

Although the idea of percolative phase transitions is conceptually fairly simple, few analytical solutions for critical parameters have been found in three dimensions. For the Ohmic case, Golden has derived the inequality $1 \leq t \leq 2$ for two and three spatial dimensions and has proposed $t = 2$ as the probable exact solution for three dimensions [5]. Other authors have obtained $t \approx 2$ using computer simulations and series expansions [6,7]. For a continuum of interpenetrating spheres, numerical analysis has consistently found $\Phi_c = 0.30$ [8–10]. Series analysis techniques have demonstrated that for nonlinear random resistor networks where the current (I)-voltage (V) relationship of resistors is given by $I \sim V^{1/n}$, the value of t increases for $n < 1$ [11–13].

Experimental attempts to determine these parameters have consisted of distributing conducting or semiconducting particles in insulating polymer or inorganic matrices [14–16]. All of these investigations have been limited in accuracy due to the inability to change Φ, the fraction of conducting material, continuously on a single sample while monitoring the conductivity change. The recent investigation by Lyons [14] has pointed out that in previous experiments the percolation threshold is subject to experimental conditions such as polymer and metal particle size, conducting particle aspect ratio, density, size distribution, and gravity. The large variance in experimental values for the threshold is attributed to these effects. The percolation threshold measured in these experiments is that of hard spheres which do not interpenetrate. Experimental values for the threshold of interpenetrating spheres have not been reported to our knowledge. With regard to nonlinear networks, no experiments have been performed to determine the critical exponents. In this Letter we report, for the first time to our knowledge, experimental values for both the percolation threshold for interpenetrating spheres and the critical exponent for nonlinear random resistor networks in the case $n = \frac{1}{2}$.

Furthermore, it will be shown that the percolation process in excimer laser irradiated polyimide provides a unique experimental method to study the percolative metal-insulator transitions of three-dimensional random resistor networks [17,18]. The process is attractive for the study of percolation theory as it allows for virtually continuous change of the volume fraction Φ and *in situ* monitoring of the conductivity. The process is also free from the constraints outlined above which have prevented accurate measurement of the percolation threshold. Close

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to the percolation threshold, the current-voltage relationship in excimer laser irradiated polyimide is nonlinear if a small applied voltage (< 10 V) is used for measurement [18] which allows the determination of the critical exponent t for a nonlinear random resistor network.

Polyimide exhibits a metal-insulator transition when irradiated with a critical number of UV excimer laser pulses of fluences greater than 20 mJ/cm^2 [17,18]. This process changes the electrical conductivity of polyimide by up to 18 orders of magnitude. The UV light is strongly absorbed by the polymer and pyrolyzes the material into conducting carbon clusters. The density of these clusters increases with successive laser shots, and a three-dimensional continuum percolation process results in the metal-insulator transition. For small applied voltages near the percolation threshold, the conduction is not Ohmic, and the current is related to voltage by $I \sim V^2$, i.e., $n = \frac{1}{2}$ [18]. As the conductivity approaches $10^{-2}\ \Omega^{-1}\,\mathrm{cm}^{-1}$ the conduction becomes Ohmic.

In our experiments, polyimide film (Kapton) of 75 μm thickness is irradiated with 30 ns (FWHM) krypton-fluoride (KrF) laser pulses (248 nm) at repetition rates from 1 to 5 Hz and fluences from 20 to 80 mJ/cm^2. A constant flow of nitrogen gas over the sample surface is maintained throughout all experiments. The KrF light passes through a diverging lens for attenuation and is then absorbed by the sample, which is kept in constant motion in a small area of the beam to ensure homogeneous irradiation. After each laser shot, an electrometer measures the resistance with a constant voltage source, and the data are stored in a computer. Contact is made with the sample through previously irradiated regions on the edge of the sample area, which are subsequently painted with colloidal silver. The contact was verified to be Ohmic up to a field of 2×10^4 V/cm. Figure 1 shows the conductivity of a sample measured in this way as a function of the number of laser shots and the volume fraction of conducting material (explained below). For these data an applied voltage of 30 V was used for the measurement such that the I-V curve is linear throughout almost the entire range. After a critical number of laser shots (350 ± 50 for this fluence of 30 mJ/cm^2), the conductivity reaches the threshold and increases from 10^{-7} to $10^{-1}\ \Omega^{-1}\,\mathrm{cm}^{-1}\,\mu\mathrm{m}$. The value of the conductivity below the threshold reflects the noise limitations in the experiment and not the actual conductivity of polyimide. Independent measurements have shown the conductivity of the polyimide to be less than $10^{-15}\ \Omega^{-1}\,\mathrm{cm}^{-1}$ below the percolation threshold [18,19]. The conductivity is also shown on a linear scale together with a fit to Eq. (1) with $t = 2.0$ and $\Phi_c = 0.3$.

Transmission electron microscopy (TEM) was used to study 12 μm thick Kapton films irradiated with differing numbers of laser shots, one of which is shown in Fig. 2. The sample shown here was irradiated 1000 times at 28 mJ/cm^2, well within the conducting phase. The sample was thinned by ion milling from the reverse side.

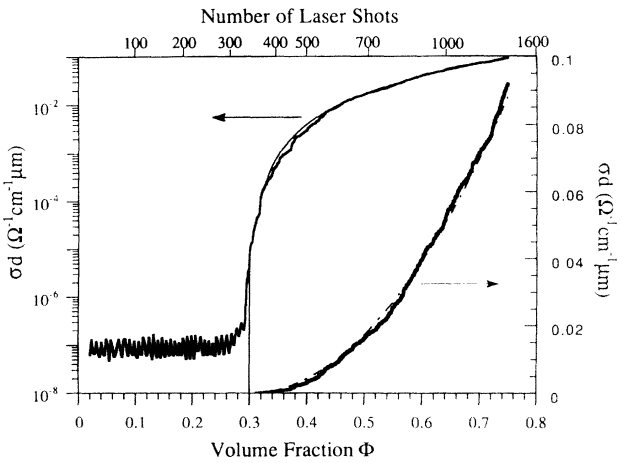

FIG. 1. Electrical conductivity as a function of volume fraction given by Eq. (3) and the number of laser shots is shown for a representative sample on a logarithmic scale and a linear scale together with theoretical curves using Eq. (1) with $t = 2.0$ and $\Phi_c = 0.3$. The theoretical curves are not visible everywhere due to the multitude of data points and the good agreement between theory and experiment. The values of conductivity in the insulating region of the transition do not represent the actual conductivity but the noise limitations of the measurement technique. For volume fractions far above threshold ($\Phi > 0.7$) the data deviate from the theoretical curve.

Here connected, interpenetrating clusters of varying size are clearly visible as the major constituent of the conducting layer. Other TEM studies were performed on cross sections of material obtained through ultramicrotomy techniques and show similar clusters. The conducting layer was measured in this way to be 1 to 2 μm thick for samples irradiated at 50 mJ/cm^2. Typical cluster sizes shown in Fig. 2, well above the percolation threshold, are about 50 nm which is considerably smaller than the thickness of the conducting layer. Dark field TEM investigations showed cluster sizes in the range of 2 to 20 nm close to the percolation threshold. The ratio of the thickness of the conducting layer to the cluster size is therefore greater than 20 over the entire conductivity range. An investigation on percolation in bounded geometries suggested that the percolation threshold is unaffected by the finite size when this ratio exceeds 10 [20]. In previous investigations we found a deviation from the three-dimensional behavior in holographically generated submicron conducting wires in polyimide [19,21]. Parallel electron energy loss spectroscopy (PEELS) and Fourier transform infrared spectroscopy (FTIR) have verified that the chemical composition of this surface layer is primarily carbon with the concentrations of nitrogen and oxygen decreasing sharply with laser irradiation [18].

In order to better understand the conduction mechanism of the conducting polymer, the temperature dependence of the conductivity was investigated. The conductivity varied with temperature according to the

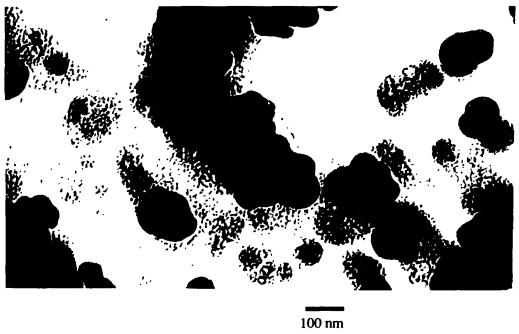

FIG. 2. TEM micrograph of the conducting layer. The sample was prepared by irradiating 12 μm foils 1000 times at 28 mJ/cm^2 and ion milling from the reverse side. The existence of approximately spherical interpenetrating conducting sites is clearly visible.

following expression:

$$\ln(\sigma) = (T/T_0)^{\gamma} . \quad (2)$$

A comparison of Eq. (2) with experiments gave a value for the exponent $\gamma = 0.25 \pm 0.05$ [18,19,21]. It has been shown that similar three-dimensional continuum percolation systems exhibit a conduction mechanism known as phonon-assisted variable range hopping [15,22,23]. The characteristic temperature dependence of the conductivity of such a mechanism is that of Eq. (2) with an exponent of $\gamma = \frac{1}{4}$ [24], which is in excellent agreement with the experimental result.

The appearance of the conduction threshold, the power law dependence of the conductivity, the identification of the variable range hopping conduction mechanism, and the microscopic geometry of the conducting layer revealed in the TEM studies provide strong evidence for the use of a three-dimensional continuum percolation model to describe the metal-insulator phase transition of the laser irradiated polyimide.

Although data such as that presented in Fig. 1 determine the critical number of laser shots unambiguously, Φ_c cannot be determined unless the fraction of nonconducting material transformed during each laser shot is known. This value can be independently determined when the change in optical transmission is measured as a function of laser shots at a wavelength of light that is highly absorbed by the conducting clusters yet transparent to the polyimide film [18,19].

The volume fraction of conducting material, Φ, is expressed as a function of a constant η and the number of laser shots N and varies between 0 and 1 according to the following relation [19,24]:

$$\Phi(N) = 1 - e^{-\eta N} . \quad (3)$$

Using the data in Refs. [18,19], η has been determined to be $(1.34 \pm 0.30) \times 10^{-3}$. We can now determine Φ_c from Eq. (3) by evaluating $\Phi(N)$ at the critical number of laser shots which was found to be 275 ± 15 at 80 mJ/cm^2. Therefore $\Phi_c = 0.31 \pm 0.06$, in good agreement with the theoretical value [8–10].

Once the critical volume fraction Φ_c is determined, the conductivity exponent t can be found by comparing experimental values such as those shown in Fig. 1 to Eq. (1). A comparison of Eq. (1), using the expression for Φ in Eq. (3) with approximately 25 sets of data such as that shown in Fig. 1, yields a value for t of 2.00 ± 0.05. The result is in excellent agreement with the recent theoretical results outlined above [5,6]. Changes in experimental conditions such as laser repetition rate and fluence had no effect on the value of the critical exponent.

In order to investigate the possibility of measuring the conductivity critical exponent t for a nonlinear current-voltage characteristic, small applied voltages were used in similar experiments to those reported in Fig. 1. Under such conditions we have measured $I \sim V^2$, i.e., $n = \frac{1}{2}$ with good accuracy [18,19]. The activation energy kT_0 was determined from Eq. (2) to be on the order of 5 meV at room temperature for conducting samples well above threshold. Values of $kT_0 = 4$ eV were measured close to the conduction threshold [18]. The correspondence between the region of high activation energy and the region of non-Ohmic conduction indicates that the origin of the nonlinearity is local to the hopping sites and can be considered a nonlinear random resistor network of the type analyzed in Refs. [11–13].

The difference in behavior of samples at low applied voltages is most clearly demonstrated in Fig. 3. In these experiments, measurements at 50 (linear regime) and at 5 V (nonlinear near threshold) were taken on the same sample. After every ten laser shots the process was stopped, and measurements were taken at each voltage. Such a method restricts accuracy in comparison to the data of Fig. 1 but dramatically illustrates that the low voltage data cannot be described by the same critical exponent as the high voltage data in the threshold region. The theoretical curve of Eq. (1) with $t = 2.0$ (drawn curve) is seen to follow the high voltage data while the theoretical curve with $t = 3.0$ (dashed curve) is seen to follow the low voltage data in the threshold region. Both sets of data follow $t = 2.0$ away from threshold. To quantitatively determine the critical exponent for the nonlinear case, measurements similar to those described for the data of Fig. 1 were performed with a small applied voltage. The exponent was then found by comparing only data near the threshold to Eq. (1). The value for the critical exponent in the nonlinear case was determined from such measurements to be $t = 2.7 \pm 0.4$ which shows the expected increase for $n < 1$. The theoretical prediction for $n = \frac{1}{2}$ is $t = 2.36$ which is within the margin of error of the experiment [11].

One might argue that each "resistor" in our network crosses over from $I \sim V^2$ to $I \sim V$ at a particular threshold voltage. This must mean that at any given external voltage some of the local resistors with large currents will behave linearly, while others, with small

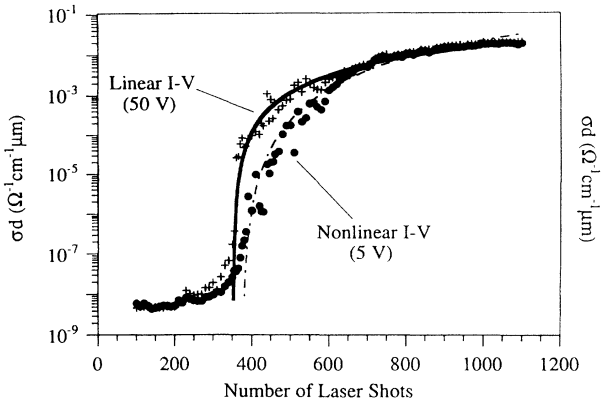

FIG. 3. Electrical conductivity is shown as a function of the number of laser shots for a single sample where the process was stopped at ten shot intervals and measurement taken at both 50 and 5 V corresponding to the linear and nonlinear regimes, respectively. For the higher voltage data the drawn line is Eq. (1) with $t = 2$, while for the lower voltage data the dashed curve is for $t = 3$. After 600 shots the two measurements become almost indistinguishable, and the $t = 2$ curve describes both sets of data well.

currents, will still behave nonlinearly. If this is the case the theory developed in Ref. [11] is not strictly applicable and should be revised accordingly [25]. The observed crossover from $t = 3$ to $t = 2$ away from threshold (Fig. 3) could be explained by this effect. Well above threshold a larger fraction of resistors can carry large currents and thus become more linear than close to threshold. For large concentrations the critical exponent should therefore approach the value for a linear three-dimensional resistor network in agreement with the experiment. Nonlinear I-V relations have been observed in other percolation systems [26], and the effects of finite size scaling provided suitable explanations. However, such explanations do not apply to the current situation when the details of the I-V characteristics are compared.

In summary, we have presented the metal-insulator transition observed in KrF laser irradiated polyimide as a method for the study of three-dimensional percolation and have measured the critical volume fraction and conduction exponent t in the linear and nonlinear regions of the transition. As is clearly shown in the data of Fig. 1, the system offers the unique ability to monitor the electrical conductivity *in situ,* while the volume fraction Φ is changed in a virtually continuous fashion. The first experimental observation of the effect of a nonlinear current-voltage relation on the conductivity critical exponent t is reported as well as the first measurement of the volume fraction for the case of interpenetrating spheres. The values obtained are in good agreement with theoretical predictions.

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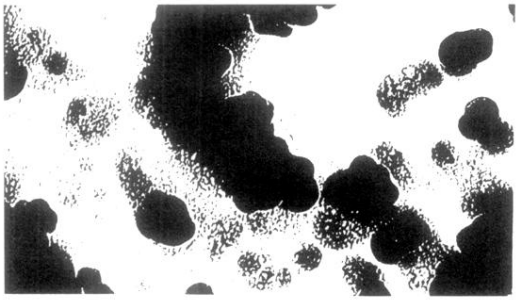
[1] D. Stauffer and A. Aharony, *Introduction to Percolation Theory* (Taylor and Francis, Washington, DC, 1992).
[2] M. B. Isichenko, Rev. Mod. Phys. **64**, 961 (1992).
[3] A. Bunde and S. Havlin, in *Fractals and Disordered Systems*, edited by A. Bunde and S. Havlin (Springer-Verlag, Berlin, 1993).
[4] B. I. Halperin, S. Feng, and P. N. Sen, Phys. Rev. Lett. **54**, 2391 (1985).
[5] K. Golden, Phys. Rev. Lett. **65**, 2923 (1990).
[6] D. B. Gingold and C. J. Lobb, Phys. Rev. B **42**, 8220 (1990).
[7] J. Adler, Y. Meir, A. Aharony, A. B. Harris, and L. Klein, J. Stat. Phys. **58**, 51 (1990).
[8] G. E. Pike and C. H. Seager, Phys. Rev. B **10**, 1421 (1974).
[9] S. B. Lee, Phys. Rev. B **42**, 4877 (1990).
[10] U. Alon, A. Drory, and I. Balberg, Phys. Rev. A **42**, 4634 (1990).
[11] Y. Meir, R. Blumfeld, A. Aharony, and A. B. Harris, Phys. Rev. B **34**, 3424 (1986).
[12] S. W. Kenkel and J. P. Straley, Phys. Rev. Lett. **49**, 767 (1982).
[13] J. P. Straley and S. W. Kenkel, Phys. Rev. B **29**, 6299 (1984).
[14] A. M. Lyons, Polym. Eng. Sci. **31**, 445 (1991).
[15] D. van der Puten, J. T. Moonen, H. B. Brom, J. C. M. Brooken-Zijp, and M. A. Michels, Phys. Rev. Lett. **69**, 494 (1992).
[16] W. Y. Hsu, W. G. Holtje, and J. R. Barkley, J. Math. Sci. Lett. **7**, 459 (1988).
[17] M. Schumann, R. Sauerbrey, and M C. Smayling, Appl. Phys. Lett. **59**, 428 (1991).
[18] T. Feurer, R. Sauerbrey, M C. Smayling, and B. J. Story, Appl. Phys. A **56**, 275 (1993). The value of the exponent in Mott's law can be fitted to the data with values other than 0.25, but these yield unphysical values for the activation energy.
[19] H. M. Phillips, Ph. D. thesis, Rice University, 1993.
[20] J. Chalupa, J. Phys. C **12**, L665 (1979).
[21] H. M. Phillips, S. Wahl, and R. Sauerbrey, Appl. Phys. Lett. **62**, 2572 (1993).
[22] V. Ambegaokar, B. J. Halperin, and J. S. Langer, Phys. Rev. B **4**, 2612 (1971).
[23] N. F. Mott, *Metal-Insulator Transitions* (Taylor and Francis, Washington, DC, 1990).
[24] V. K. S. Shante and S. Kirkpatrik, Adv. Phys. **20**, 325 (1971).
[25] This was kindly pointed out to us by A. Aharony who has discussed a similar crossover situation in Phys. Rev. Lett. **58**, 2726 (1981).
[26] K. K. Bardhan and R. K. Chakrabarty, Phys. Rev. Lett. **72**, 1068 (1994), and references cited therein.



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