Percolation and metal–nonmetal transition during laser evaporation of condensed media

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The optical emission and the microwave conductivity of dense vapor near the surface of powdered-mixture targets have been studied experimentally as a function of the mixture composition. The behavior is found to be characteristic of percolation. The high-frequency conductivities of the oxide and metal percolation clusters are comparable in order of magnitude. © *1994 American Institute of Physics.*

During the evaporation of a metal, a gas phase with a density comparable to that of a liquid becomes metallic (an "expanded metal"). [1] The high conductivity results from an overlap of the electron clouds of the atoms. The "metal–nonmetal" transition can be interpreted well on the basis of the concept of percolation as developed for disordered media. This concept has previously been used successfully to describe the electrical conductivity of doped semiconductors. [2] In general, the possible formation of percolation clusters during the evaporation of nonmetallic, condensed media has not been considered, and certainly there has been no study of the effect of such structures on the conductivity of a vapor–gas mixture. The dense, low-temperature plasma, which arises during the application of laser beams to condensed media, is nevertheless an effective source of a wide spectrum of particles, including compact clusters consisting of a large number of atoms. [3] Fractal structures are also observed in laser experiments, but their formation is associated with an aggregation of tiny cooled droplets, rather than a percolation. [4] The existence of percolation structures in a dense plasma seems obvious at the outset, and it is supported by (in the case of silica gel, for example) calculations by the molecular-dynamics method. [5] However, the existence of these structures has not yet been proved experimentally.

The formation of stable clusters in a liquid or a nonideal plasma is opposed by the participation of subunits in a disordered Brownian motion. In such cases, a dynamic percolation model holds, and the existence of percolation structures can be seen by carrying out observations over times shorter than the restructuring time. [6] Studies of the dc conductivity, which have been used successfully to learn about the static percolation model, are obviously unsuitable for studying dynamic percolation structures. In this case an ac experiment is necessary, and the frequency must be fairly high. A lower boundary on the frequency is set by the residence time of an individual unit in a cluster. The experimental results reported below were obtained at frequencies in the microwave range (10^{10} Hz) and in the optical range (6×10^{15} Hz).

On the other hand, studies [7] of the optical properties of disordered media, consisting

of a metal and an insulator (island films), have shown that, as the extent of coverage is varied, a metal–nonmetal transition is seen only at low frequencies, at which the dc approximation is valid for the conductivity. In a field of sufficiently high frequency, the growth of clusters in the range of sizes greater than the wavelength of the radiation ceases to affect the conductivity. The role of small clusters, on the other hand, increases, since a capacitive coupling between (in particular) dangling parts of percolation structures comes into play at frequencies in the optical range.

The dc conductivity of a two-phase system near the percolation threshold p_c (p is the concentration of the conducting phase) is a function of the relative distance $\tau=(p-p_c)/p_c$, $|\tau|\ll 1$. It is characterized by critical exponents t and q in accordance with the expressions [8]

$$\sigma\approx\sigma_{\rm dc}^{m}\tau^{t}, \quad \tau>0, \quad t(d=3)=1.7,$$
$$\sigma\approx\sigma_{\rm dc}^{i}|\tau|^{-q}, \quad \tau<0, \quad q(d=3)=0.7.$$

The conductivities of the different phases satisfy $\sigma_{\rm dc}^{m}\gg\sigma_{\rm dc}^{i}$ where d is the dimensionality of the space. Above the percolation threshold, the increasing conductivity is due to a growth of a giant percolation cluster. Below the threshold, the resistance is governed by a parallel connection of single dangling bonds. In the case of an alternating current, the real part of the conductivity varies in accordance with the Drude–Lorentz law, and a term $\sigma^{i}\approx\omega^{2}C^{2}/\sigma_{\rm dc}^{m}$ where ω is the frequency and C is the capacitance of an individual dangling bond, is added to the conductivity of the poorly conducting phase, $\sigma_{\rm dc}^{i}$ (Ref. 7). At a finite ratio of the conductivities of the phases, the transition is smeared out, and the critical exponent for the effective conductivity becomes $y=(t-q)/2\approx 0.5$ according to Ref. 8, while the theory of Ref. 9 predicts a linear behavior of the conductivity near the threshold.

It was shown in Ref. 10 that a laser discharge initiated and sustained by laser light near the surface of, or in the interior of, an insulator containing oxygen is an effective source of fractal matter. The high rate at which macroscopic fractal structures form in the discharge cannot be explained by the model of a diffusion-limited cluster–cluster aggregation. [11,12] The possibility of a model of percolation growth was suggested in Ref. 10. The results reported below indicated that percolation structures do indeed exist in the plasma of a laser discharge. So far, we have studied about 50 different compounds, including some composites. The results show that the concentration dependence for the rf conductivity of the discharge plasma is usually a characteristic percolation dependence and correlates with the concentration dependence for the effectiveness of fractal formation. A sharp increase in the absorptivity and emissivity of the plasma (these characteristics are directly associated with the rf conductivity) is observed when a threshold is exceeded, either as the density of the vapor-gas phase changes as material is evaporated into a closed volume or upon a change in the concentration of the conducting component (in particular, a metal or oxide).

In the experiments we studied the emissivity of a discharge plasma, which has a continuous emission spectrum, in the optical range. In the rf range we studied the absorptivity of a plasma. The two signals were recorded simultaneously. For this purpose, a target consisting of a pressed tablet of a mixture of powdered substances, positioned

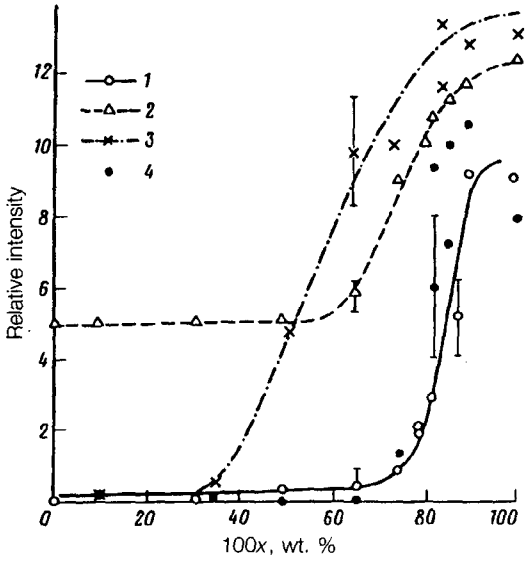

FIG. 1. Concentration dependence of the emission intensity (1), of the intensity of the scattered laser light (2), and of the microwave absorption during (3) and after (4) the laser pulse for a discharge plasma near the surface of a target consisting of an $(AlF_3)_{1-x}$–Al_x mixture.

outside a microwave waveguide ($\lambda = 3$ cm), beyond its wide wall, was illuminated by the laser beam. The incident laser beam and the flux of evaporated material propagating opposite the laser beam passed through holes at the center of a wide wall of the waveguide. The optical emission being studied also passed through these holes. A reflection arrangement was used to measure the microwave absorption signal. [13] A molybdenum foil was pressed against the target surface to stabilize the initial conditions (in particular, the heating of the material). The target material was diluted with insulators which do not exhibit intrinsic emission with a continuous spectrum under our experimental conditions. These insulators were usually halides of metals whose atoms (or the molecules of whose oxides) participate in clustering. As a rule, the buffer gas was air under standard conditions. Changes in the composition of this buffer gas (hydrogen, nitrogen, CO_2, inert gases, etc.) and changes in its temperature (0–100°C) or pressure (10^{-3}–2 atm) did not cause any substantial changes in the optical properties of the plasma during rapid evaporation. Some special experiments carried out at various power densities of the laser beam, over the range 10^6–10^7 W/cm ^{2}, to determine the effect of heat evolution in the plasma on the emissivity of the plasma, revealed no fundamental changes in the percolation behavior.

The signal representing the emission of the discharge plasma reproduces the shape of the incident laser pulse, with a length ~10 ms, in a first approximation. The following cases occur in the rf range: During the illumination of oxides, the microwave signal coincides with the emission signal. During the illumination of a binary mixture of powders of the metal and its halide salt, the absorption at the time at which the laser pulse is applied is accompanied by a second peak, almost 10 ms after the end of the applied pulse. Figure 1 shows the concentration dependence of the intensity of the intrinsic emission of the plasma, with a continuous spectrum (1), that of the scattered laser light (2), and that of the microwave absorption during (3) and after (4) the laser pulse. These results were obtained during the illumination of targets with compositions Al_x–$(AlF_3)_{1-x}$.

In a metal percolation cluster, a continuous emission spectrum arises as the result of transitions in the continuous spectrum of excitations of a quasiatom whose valence-electron states contain an admixture of asymptotically free motion. [1] The onset of emission in the plasma of a laser discharge can be assumed to result from the formation of percolation clusters (metallic in the case at hand). Because of the correlation between the signals representing the emission and the delayed microwave absorption, this absorption can be linked with percolation clusters. At a high temperature during the application of the laser pulse, the corresponding microwave-absorption signal (first) is masked by the absorption of radiation in the metallic droplet fraction and (second) may be reduced substantially, because of the short residence times of the metal atoms as units of the percolation structure. The temperature decay after the laser pulse naturally erases the emission and increases the residence time. As a result of the effective growth of percolation clusters, the conductivity of the vapor–gas phase increases. A further consequence is an increase in the intensity of the microwave-absorption signal. The disappearance of the latter signal results from expansion of the material out of the peripheral region of the plasma burst and from the deposition of percolation clusters on the waveguide walls. Confinement of the expansion region inside the waveguide leads to a significant weakening of the microwave-absorption signal observed after the end of the laser pulse. Individual metal droplets and aggregate clusters of these droplets exist in the flux of evaporated material and rapidly move away from the target surface.

Comparing plots 2 and 3 in Fig. 1, we conclude that the concentration of scattering centers does not track the concentration of the droplet fraction. The behavior of the scattered-light intensity can also be explained under the assumption of a percolation transition, an analog of a second-order thermodynamic phase transition. In this case, seed clusters in the prethreshold region correspond to density fluctuations in the vicinity of the critical point. The average size of these clusters, R, is described by the following expression according to percolation theory: [14]

$$R \sim \tau^{-\gamma}, \text{ where } \gamma(d=3)=1.74.$$

The experimental results are described satisfactorily by this value of the critical exponent if the threshold concentration is found from curve 1 in Fig. 1.

The experimental results show in Fig. 2 indicate that percolation clusters with an rf conductivity not substantially different from that of metallic percolation clusters arise in the dense vapor of typical insulators. The experimental results found for various compositions of the target support the assertion that the conducting phase arises from an overlap of the electron clouds of the oxide complexes. We would like to point out the following aspects of the experiments with oxide compounds:

1) The droplet fraction in the case of the insulators naturally does not contribute to the active conductivity.

2) The residence time in the oxide percolation structures is longer than that in the metal structures, and a microwave-absorption signal can be observed during the application of the laser pulse.

3) The oxide percolation structures exhibit a significant conductivity only at high temperatures.

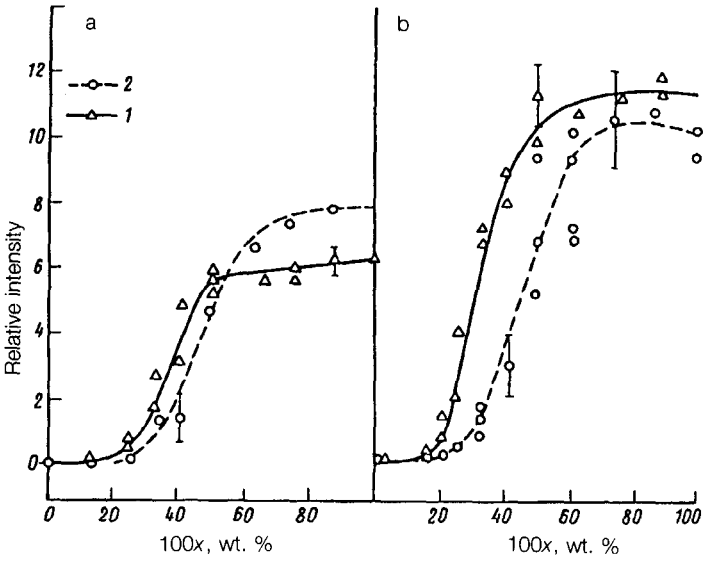

FIG. 2. Concentration dependence of the emission intensity (1) and of the microwave absorption (2) for a discharge plasma near the surface of a target consisting of a halide–oxide mixture. a—$(MgF_2)_{1-x}$–$(MgO)_x$; b—$(AlF_3)_{1-x}$–$(Al_2O_3)_x$.

The latter circumstance may be due to a convolution (restructuring) of percolation structures with a fractal dimensionality $d_f = 2.5$ with respect to their elastic skeleton [15] ($d_f = 1.5$), which would lead to the formation of fractal aggregates of lower dimensionality ($d_f = 1.5$), but consisting of larger structural elements [10] ($r_0 \sim 10$ nm). Oxide blocks of nanometer size are characterized by insulating properties, and clusters of them, like the droplet fraction, do not contribute to the active conductivity.

[1] A. A. Likal'ter, Usp. Fiz. Nauk **162**, 119 (1992) [Sov. Phys. Usp. **35**, 591 (1992)].
[2] B. I. Shklovskiĭ and A. L. Éfros, *Electronic Properties of Doped Semiconductors* [in Russian] (Springer-Verlag, New York, 1984).
[3] E. E. B. Campbell *et al.*, J. Chem. Phys. **93**, 6900 (1990).
[4] A. A. Lushnikov *et al.*, Dokl. Akad. Nauk SSSR **292**, 86 (1987) [Sov. Phys. Dokl. **32**, 45 (1987)].
[5] J. Kieffer and C. A. Angell, J. Non-Crystalline Solids **106**, 336 (1988).
[6] M. I. Ozhoban, Zh. Eksp. Teor. Fiz. **104**, 4021 (1993) [JETP **77**, 939 (1993)].
[7] Y. Yagil *et al.*, Phys. Rev. B **43**, 11342 (1991).
[8] A. E. Morozovskiĭ and A. A. Snarskiĭ, Zh. Eksp. Teor. Fiz. **104**, 4059 (1993) [JETP **77**, 959 (1993)].
[9] P. A. Lee and T. V. Ramakrishnan, Rev. Mod. Phys. **57**, 287 (1985).
[10] N. E. Kask and G. M. Fedorov, Kvant. Elektron. (Moscow) **20**, 527 (1993) [Quantum Electronics **23**, 453 (1993).
[11] P. Meakin, in *Phase Transition and Critical Phenomena*, ed. by C. Domb and J. L. Lebowitz (New York, 1988).
[12] B. M. Smirnov, Usp. Fiz. Nauk **161**, 171 (1991) [Sov. Phys. Usp. **34**, 526 (1991)].
[13] N. E. Kask *et al.*, Fiz. Khim. Stekla **11**, 68 (1985).
[14] D. Stauffer, in *Introduction to Percolation Theory* (Taylor and Francis, London, 1985).
[15] A. Chhabre *et al.*, in *Fractals in Physics*, ed. by L. Pietronero and E. Tosatti (Amsterdam, 1986).

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