

# Switching behavior of plasma polymer films containing silver nanoparticles

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A reversible electronic switching effect has been observed in plasma polymer films with embedded silver nanoparticles. The electrical and nanostructural properties of the films have been investigated, and three different structure types were observed: metallic, percolation, and dielectric. While for the metallic and dielectric types, respectively, metallic conduction and thermally activated tunneling can be identified as the dominant electronic conduction mechanisms, switching appears only in percolation structures. These drastic, abrupt changes of up to six orders of magnitude in the current–voltage behavior are highly reversible for these nanocomposite materials, and are defined as threshold switching. © 2003 American Institute of Physics. [DOI: 10.1063/1.1622990]

Generally, the electrical properties of plasma polymer/metal composite films can be classified according to their nanostructures into three different categories: metallic, dielectric, and transition or percolation.<sup>1</sup> The electrical properties of such composite films are strongly linked to the particles' nanostructure, and theoretical conduction models for discontinuous metal films can be applied below the percolation threshold, where the particles in the matrix material are isolated from each other (dielectric regime). The conductivity mechanism here is characterized by electron tunneling from one metal particle to the neighboring one in a thermally activated tunneling process. The electrical dc conductivity is on the order of  $\sigma \leq 10^{-8} \Omega^{-1} \text{cm}^{-1}$ . Above the percolation threshold, where the particles form a metallic continuum with dielectric inclusions, metallic conduction takes place, with conductivity in the range of  $\sigma \geq 10^{-2} \Omega^{-1} \text{cm}^{-1}$ . However, the conductivity is lower than that of bulk metal, since the mean free path of the electrons is reduced due to additional electron scattering. The transition region from the metallic to the dielectric state occurs at a critical metal fraction with conduction characterized by percolation models. In this case, the particles form a contact network, or percolation path, and relatively small changes in the metal content cause relatively large changes in the film conductivity. The temperature coefficient of resistance is negative for samples of dielectric type and slightly positive for metallic.

Recently, the fabrication of periodically arranged, wire-like particle structures in plasma polymer films with embedded gold and silver nanoparticles was described.<sup>2</sup> These structures were induced by irradiation with linearly polar-

ized, ultrashort laser pulses, and the films show anisotropic optical and electrical properties in the laser treated areas. In this communication, however, we report on the electrical properties of plasma polymer films containing silver nanoparticles, and, in particular, on their switching behavior, which is attributed to a specific nanostructure near the percolation threshold.

The films were made by silver evaporation and plasma polymerization as a multilayer system on a quartz substrate. The monomers used for the 50 Hz plasma polymerization were hexamethyldisilazane (HMDSN) and benzene, and no significant difference in electrical behavior was observed for the two matrix materials. The resulting films were characterized by two-dimensional silver particle distribution of the sizes and shapes shown to the right in Fig. 1. Because of the plane particle distribution, the nanostructure can be characterized by an area filling factor  $f_a$  (defined as the area covered by the silver/total film area).  $f_a$  can be determined by computer-aided image analysis of the transmission electron microscopy (TEM) images. Besides the current–voltage ( $I$ – $V$ ) diagram, Fig. 1 shows typical TEM micrographs of the different nanostructural types (top: metallic, middle: percolation, bottom: dielectric). Cross-sectional TEM (not presented here) demonstrated that the particles are dispersed in one plane. Thickness  $d$  and  $f_a$  values were measured for these films that consisted of silver nanoparticles embedded in the plasma polymer made from HMDSN, giving  $d=60$  nm at  $f_a=0.89$  in the metallic region,  $d=32$  nm at  $f_a=0.78$  near the percolation threshold, and  $d=26$  nm at  $f_a=0.42$  in the dielectric regime. Due to the specific film fabrication, which is explained in more detail in Ref. 3, it is possible to produce films from a single film deposition with continuously vari-

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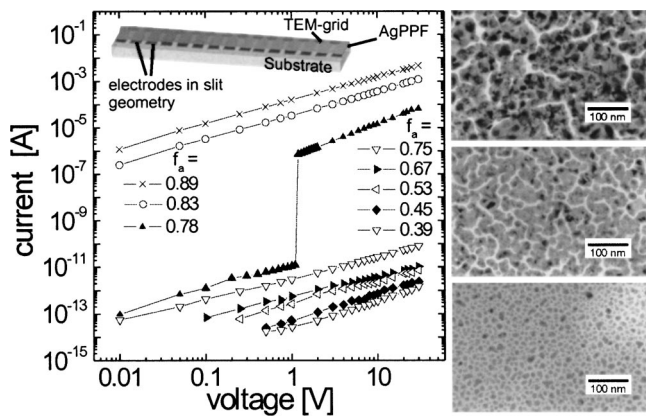


FIG. 1. Left:  $I$ - $V$  characteristics of a plasma polymer film containing silver nanoparticles (AgPP film) with different area filling factors  $f_a$ . Top left: Sample setup: Coplanar electrode arrangement (slit dimensions  $500 \mu\text{m} \times 6 \text{mm}$ ); placement of TEM grids is matched to film positions (slits) for the electrical measurements. Right: TEM micrographs of different nanostructural types (dark: metal; light: plasma polymer).

able proportions of silver, thereby enabling the investigation of different nanostructural types with the same matrix properties. For the electrical investigations, quartz substrates were prepared with platinum thin film electrodes before actual deposition (see Fig. 1 top left). For the TEM investigations, the carbon-deposited TEM copper grids were also placed on the substrate before film deposition in positions similar to these for the electrical measurements. The electri-

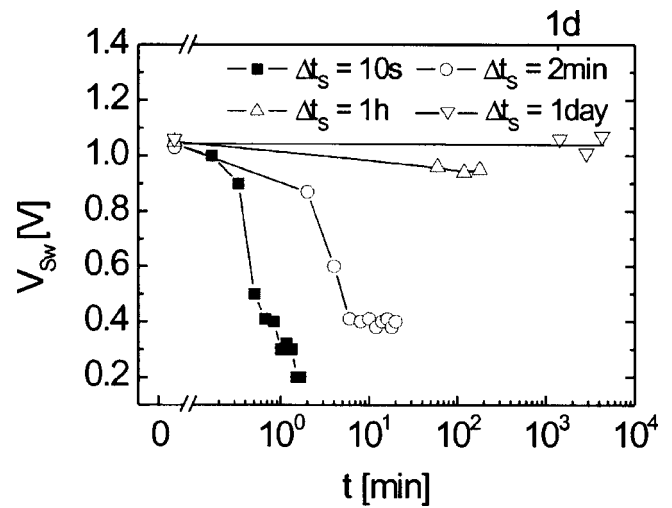


FIG. 3. Threshold voltage  $V_{sw}$  vs time between successive  $0 \text{V} \rightarrow 2 \text{V}$  measurements;  $\Delta t_s$  is the time between two measurements.

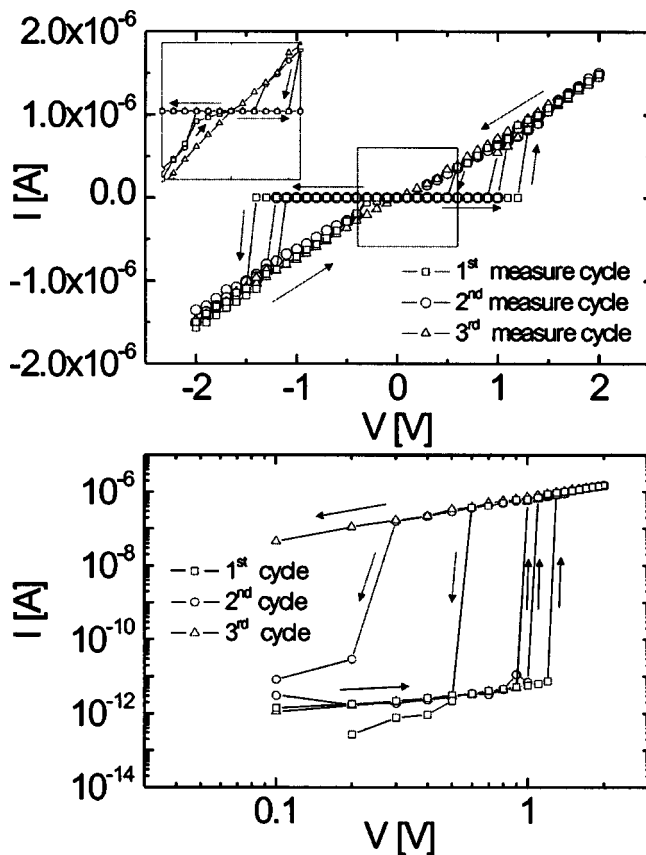


FIG. 2.  $I$ - $V$  characteristics of three  $-2 \text{V} \rightarrow 2 \text{V} \rightarrow -2 \text{V}$  measurement cycles one after another. Top: Linear plot; bottom: log-log form.

cal characteristics ( $I$  vs  $V$ ) were measured with a Keithley SMU 236 source-measure unit in a two-point arrangement. The diagram in Fig. 1 clearly distinguishes the three main structural types by means of the  $I$ - $V$  characteristics. While the characteristics of  $f_a$  greater than or less than 0.78 follow Ohm's law, the plot for  $f=0.78$  shows a jump of about six orders of magnitude. Obviously, an abrupt change in the dominant conduction mechanism occurs; it is characterized and discussed below.

Figure 2 shows the  $I$ - $V$  behavior over three  $-2 \text{V} \rightarrow 2 \text{V} \rightarrow -2 \text{V}$  measurement cycles for a typical switching sample. To show that the switching effect is independent of the current direction, three complete cycles are presented linearly in the upper diagram. From  $-2 \text{V}$  to  $0 \text{V}$ , the first cycle characteristic shows ohmic behavior, which changes at about  $-0.2 \text{V}$  (see zoomed area). This could also be observed for the second cycle, but not for the third. The following  $0 \rightarrow 2 \text{V} \rightarrow 0$  sequence is depicted more explicitly in the log-log plot in Fig. 2. The sample has low conductivity (OFF state) below the threshold voltage, and switches to an ohmic ON state (high conductivity) at the threshold field strength. Voltage limits of  $\pm 2 \text{V}$  were chosen as final values to avoid excessive stress on the samples, but measurements up to  $30 \text{V}$  have shown that the films show stable ohmic behavior in the ON state. On the downward swing ( $2 \text{V} \rightarrow 0$ ), a jump also occurs at  $0.4 \text{V}$  in the first cycle and at  $0.2 \text{V}$  in the second, but it completely disappears in the third. For further measurement cycles, there were no more "downward" conductivity jumps observed. Identical  $I$ - $V$  progressions of the switching behavior are obtained for downward ( $2 \text{V} \rightarrow 0 \text{V}$ ) and upward ( $0 \text{V} \rightarrow 2 \text{V}$ ) measurements, but only when the sample was tested right after deposition (a new sample) or after a sufficiently long discharge (grounding) time. In those cases, a threshold voltage of about  $\pm 1 \text{V}$  was typical for most of the deposited films. The dependence of the threshold voltage magnitude was determined (Fig. 3) as a function of the time between subsequent measurement cycles and the number of cycles. As shown in Fig. 3, the threshold voltage  $V_{sw}$  is nearly constant for measurements separated by long

times ( $\Delta t_s = 3$  days, 4 measurements), but decreases with subsequent testing if measurements are carried out quickly one after another (e.g., for  $\Delta t_s = 10$  s, 11 measurements).

Observations of such changes in conductivity have been reported in the literature for similar thin film materials and they can be divided into two general categories:<sup>4,5</sup> (i) threshold switching, in which electrical power is required to maintain the ON state and (ii) memory switching, in which both states (ON and OFF) can be maintained without electrical power. The changes in conductivity can be either structural, involving material transport, or electronic.<sup>4,5</sup> One of the causes of switching in pure plasma polymer films could be the formation of metal structures (bridges) between the electrodes due to diffusion of electrode material through the plasma polymer.<sup>6</sup> A model for such thermally induced switching phenomena in elastic polymer films is explained in Ref. 7 based on jet evaporation of electrode material and Joule heating which melts the filamentary bridge. Another structural explanation for these effects is the formation of amorphous conductive carbon paths within the plasma polymer.<sup>6</sup> But the relatively high reversibility of the threshold switching observed here argues against these models. Up to a few hundred switching operations have been observed for some samples, and it seems implausible that structural changes of the metal particles, i.e., coalescence into the conductive path and filamentary breakage caused by thermal mechanisms, could be responsible for such highly reversible switching over so many cycles, particularly if one considers polymer separation of the particles.

We have been working on the development of a purely electronic model of switching in granular metals based on a reversible change between two different conduction mechanisms, as described in Refs. 8–10. Under low-field conditions, when the electric field energy is much smaller than the thermal energy of the charge carrier (i.e.,  $e\Delta V \ll kT$ , where  $e$  is the electronic charge,  $k$  is the Boltzmann constant,  $T$  is the absolute temperature, and  $\Delta V$  is the interparticle gap potential), conduction is by thermally induced electron tunneling. For high fields ( $e\Delta V > kT$ ), the main conduction process is field-induced tunneling. At sufficiently high fields, where  $e\Delta V$  becomes comparable to the height of the tunneling barrier,  $\phi$ , Fowler–Nordheim field emission is expected to become dominant. The differences in conductance between these mechanisms would cover several orders of magnitude. Our modeling efforts focused on the driving mechanism for an abrupt transition between these mechanisms, which might be expected to coexist with a continuous shift from one to the other.

But are these conduction models applicable to the plasma polymer/metal particle system presented here? First of all, the differences in nanostructural properties must be emphasized. In contrast to these films, those in Refs. 9 and 10 had three-dimensional particle distributions and were measured in a sandwich configuration. Also contrary to the

results reported here, the switching effect was observed for different metal proportions. The switching effect in our films could be found only for samples with a specific proportion of silver. This nanostructure ( $f_a = 0.78$ ) is characterized by long, almost continuous particles, but with no conductive metallic path formed between the electrodes. So we assume that there is still a gap of 2 nm or less between the particles, and that an internal field of up to  $10^7$  V/cm is applied between the metallic particles when voltage of 1 V is applied between electrodes. Electrical field strengths of such orders of magnitude can provide electrons with sufficiently high energy to escape from the metal by field emission.<sup>11</sup> The metal–polymer potential barriers also become deformed by decreases in height and width of the potential barrier, so that, at sufficiently high field, electrons can tunnel through the potential barrier at the Fermi level. Relatively high current densities would occur in this high conductance state.

The idea of an electronic process is mainly supported by the relatively high reversibility of the switching effect, but there are still unresolved questions; e.g., it is not clear why the  $I$ – $V$  thresholds differ on the positive and negative voltage slopes. Since the threshold voltage and the sequence of the  $I$ – $V$  characteristics are functions of both the number of switching operations and the switching frequency, relaxation processes must be taken into account. For example, residual charges in the matrix or substrate<sup>12</sup> would explain the variation of the threshold on the cycle time. However, structural changes cannot be categorically eliminated, because the number of switching operations is not infinite. The question of whether the switching effect is caused by structural changes could possibly be answered by an *in situ* TEM experiment, but it would demand a microscopic electrode and film arrangement to observe the relevant area. Such an arrangement is hard to realize: changing the sample setup and the electron beam itself would furthermore act as a flood source of charge, and possibly dominate the whole experiment. Further investigations of the switching mechanism are in progress, specifically of thermal influences on it.

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