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## QTuE32

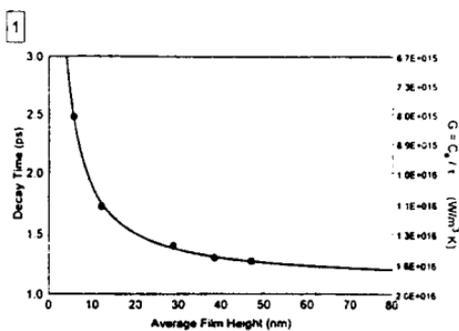
### Time-resolved carrier dynamics near the insulator-metal transition

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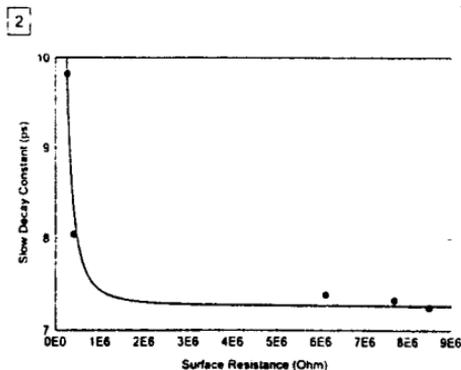
The study of insulator-metal transitions (IMTs) can provide insight into the dynamical properties of complex, disordered systems.<sup>1</sup> Specifically, the subtleties of phenomena like carrier localization and transport in systems such as conducting polymers and colloidal metal films can be probed and elucidated. This paper reports the results of optically excited carrier dynamics near the IMT in a series of thin films composed of 12-nm colloidal gold particles and a series of thin polyaniline (PANI) films of varying conductivity. Carrier lifetimes and dynamics have been probed directly by time-resolved laser spectroscopy measurements. Additionally, the films' mesoscopic structure has been determined with atomic force microscopy (AFM). Correlations are made between film structure, carrier dynamics, and conductivity. The issues of carrier localization, transport, and scattering are addressed.

The Au colloidal films, which vary in thickness from approximately 10 to 60 nm, and proportionally in domain (or aggregate) size, exhibit structurally dependent hot-electron lifetimes.<sup>2</sup> As seen in Fig. 1, the lifetimes range from 1–3 ps and decrease with increasing film thickness and greater colloid aggregation and conductivity. A simple model for the electron-phonon coupling constant can be used to account for the dependence of the hot-electron lifetime on the films' structure. This model also allows for interpolation and extrapolation to predict electron-phonon relaxation dynamics across a range of colloidal film thicknesses. Two competing phenomenon, inelastic surface scattering, which tends to increase electron-phonon coupling with decreasing domain size and electron-oscillation phonon resonance, which tends to decrease it, are shown to both contribute to the hot carrier lifetimes as a function of aggregate size. The relative contributions of each of these processes has been determined and agrees with predicted trends.<sup>3,4</sup> Finally, the results are shown to be consistent with the percolation mechanism of DC electrical conductivity that is based on activated hopping.<sup>5</sup>

Thin (~40 nm) polyaniline films, doped with camphorsulfonic acid and spin cast from chloroform solutions, were prepared in a range of conductivities by secondary doping with m-cresol vapor. Two time scales for optically excited carrier relaxation have been measured directly.<sup>6</sup> The first component, an exponential decay of ~50 fs, accounts for 99.95% of



QTuE32 Fig. 1 Colloidal Au films. Experimentally determined time constant,  $\tau$ , and e-ph coupling constant,  $G$ , shown as a function of AFM measured average film height, data points. The solid curve is the results of a NLS fit of the time constant data according to  $\tau = C_e/G$ , with  $G \propto 1/\Lambda$  and  $\Lambda = \Lambda_B + K/\langle h \rangle$ , where  $C_e$  is the electron heat capacity,  $\Lambda$  is the effective electron mean free path, and the subscript  $B$  refers to the bulk limit,  $K$  is a proportionality constant, and  $\langle h \rangle$  is the average film height.



QTuE32 Fig. 2 PANI films. Experimentally determined slow time constant,  $\tau$ , shown as a function of the surface resistance,  $R$ , measured with use of the 4-point probe method, points. The solid curve is the result of a NLS fit of the data to the function  $\tau = a + k/R^2$ , where  $a = 7.26$  ps and  $k = 1.81 \times 10^8$  ohm<sup>2</sup> ps.

the carrier relaxation. A second relaxation component, an exponential decay ranging from 7–10 ps, has been found to be depend on the film's conductivity. As shown in Fig. 2, the time constant for this component increases with decreasing resistivity and mesoscopic film homogeneity, as determined with an AFM. These results are consistent the presence of two distinct types of carriers in PANI that have independent localization lengths and scattering times. Further, the present results corroborate the recent description of PANI's IMT as a result of percolation and its relationship to disorder and localization.<sup>1</sup>

Both of these studies have implications for the design and development of devices. For example, the development of optoelectronic devices necessitates a working understanding of the relationship between structural features and performance characteristics. The results reported herein suggest a guide for the design of optoelectronic devices with synthetically tunable hot-carrier lifetimes.

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