Amorphous Carbon (a-C:H): a Mono-Elemental CerMet

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Amorphous carbon films, deposited by plasma enhanced chemical vapor deposition (plasma-CVD) or sputtering are very often treated analogous to amorphous silicon (a-Si:H), a semiconductor meanwhile very commonly used for electronic (display) or photovoltaic applications. However, due to the vast range of properties the materials are sometimes called plasma polymers of diamond like carbon.

In our investigations we were focussing on the electrical and optical properties of these materials. Just by changing the input power leading to self-bias voltages of between 100 and 1000˚V, we were able to change the conductivity of such deposited films by 10 orders of magnitude (between 10^{-12} and 10^{-2} S cm^{-1}) [1]. However, as already reported in this conference [2], at the same time the optical (as well as the mechanical) properties change. Whereas the films deposited at 100 V are transparent (and "soft"), their color changes steadily to a very deep black for the highly conductive and extremely hard as well as chemically resistant films.

As reported before there is a very strong correlation of the optical "absorption edge" and the conductivity of the films [3]. However, describing the optical properties in terms of an absorption edge as expected for a classical semiconductor is misleading. Indeed, adding "doping gases" into the deposition chamber leads to a strong increase of the conductivity of the films. However, this can also be achieved by adding inert gases such as argon, which do certainly not lead to a classical doping of carbon [4].

It was shown in further investigation that the electrical properties can best be described by a multiphonon hopping mechanism as developed by Shimakawa and coworkers [5]. Even the most surprising feature of this model, a characteristic temperature at which the conductivities of all samples become equal, is in perfect agreement with our data as determined for a vast number of samples measured in the temperature range between 80 and 550 K. All least square fits to these data point to conductivities between 0.1 and 10 S cm^{-1} at 1500 K, although the room temperature conductivities of these samples vary by 10 orders of magnitude.

A careful analysis of the optical parameters of the films [6] as determined by reflection, transmission and photothermal deflection measurements led to the surprising result that the absorption behavior below an absorption coefficient of 10^{-4} cm^{-1} can be fitted very well by a simple power law. Extrapolating the absorption to lower excitation energies suggests an increase of the density of states at the Fermi level accompanying the increase of the electrical conductivity with increasing self-bias voltage or "dopant" concentration.

Structural investigations were performed by AFM and STM measurements on the surface of these films [7]. Thereby well defined graphite clusters were identified by STM measurements on the better conductive samples. The clusters show a preferred orientation with its planes parallel to the growth direction of the film (i.e. perpendicular to the film itself), an anisotropy afterwards confirmed by ESR measurements.

In order to get volume informations of the films a detailed NMR study was performed on powder samples prepared by depositing films on aluminum foils afterwards dissolved in sulfuric acid. Here, also ^{13}C enriched samples were prepared by depositing films from ^{13}C-enriched ethylene. Various sophisticated solid state NMR techniques were applied in order to get informations on the graphite cluster sizes by analyzing the coupling and decoupling rates of protons in the sp^3 matrix of the film and the sp^2-^{13}C inside the graph-

ite clusters. These techniques will be be presented in the talk. Thereby a structure model for our a-C:H films was confirmed as shown in the figure below. According to this model the optical properties of the films are solely determined by the graphite cluster size. Multi phonon excitation followed by tunneling of excited charge carriers through the surrounding sp^3-carbon matrix into a neighboring cluster limited by the tunneling distance then determines the conductivity of the sample [8].

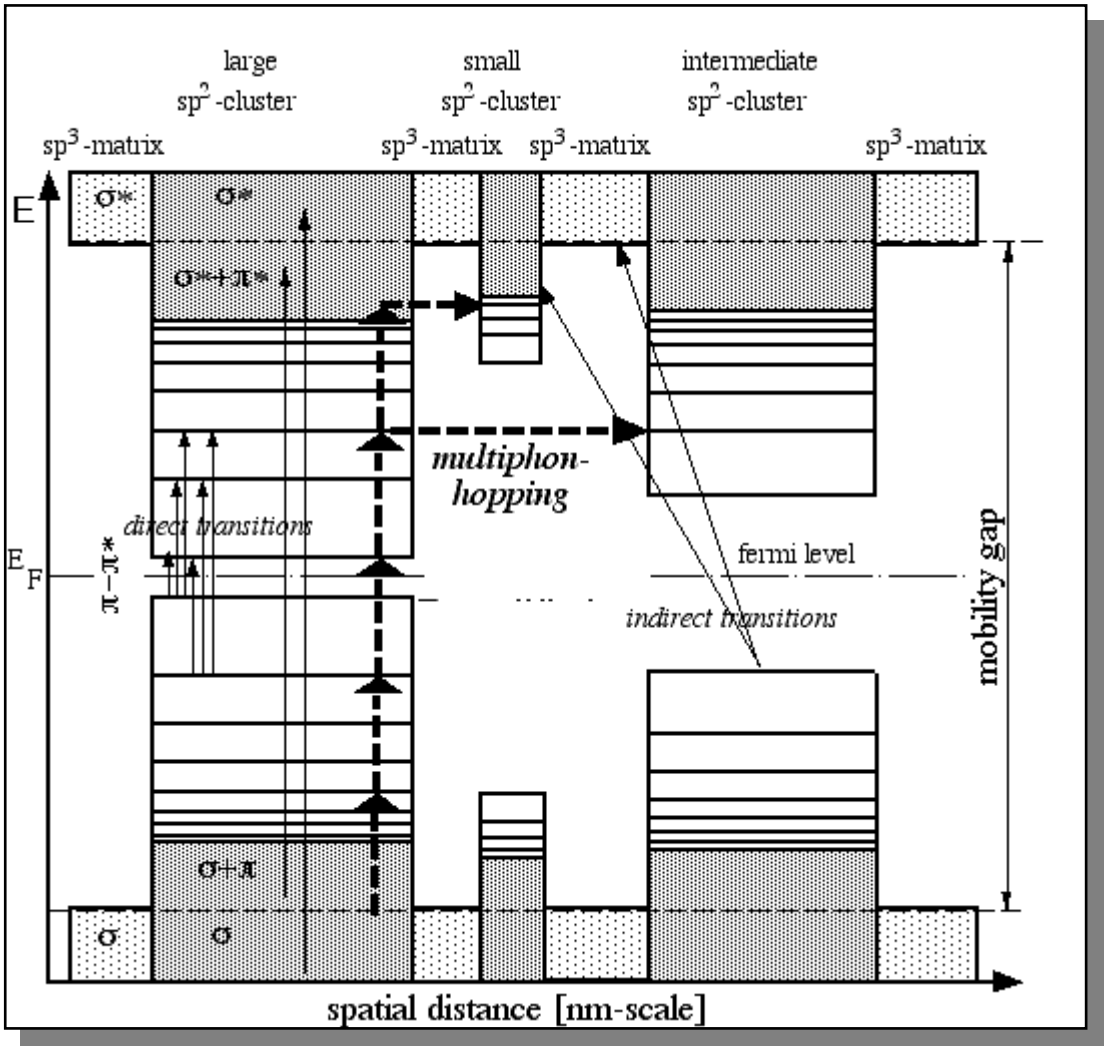

Figure: structure model of amorphous carbon cermets

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