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Preparation and electrophysical properties of the cryocondensates of lead nanoparticles and carbon dioxide

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Carbon dioxide has been found to affect the morphology and mean size of lead nanocrystallites.

Metal clusters and nanoparticles display unique size-dependent physicochemical properties that find use for performing unusual chemical reactions and creating novel catalytic and sensor nanomaterials.[1,2] Cryochemical methods are successfully used to obtain and modify nanomaterials.[2,3] For example, low-temperature methods were used to obtain ammonia-sensitive poly(*para*-xylylene) films containing lead nanoparticles.[4] In the absence of poly(*para*-xylylene), nanostructural lead films also possessed sensitivity.[5] When the specimens were heated from 80 to 300 K, the microstructure underwent changes that started at $T \approx 200$ K [$1/3T_m$(Pb), where T_m is the melting point of the metal]. The film sensitivity was shown to depend on the structure and specimen preparation conditions.[5]

In order to control the microstructure of lead condensates and to increase the porosity and specific surface of nanoparticles, we used cryococondensation with an inert gas followed by sublimation at $T \approx 200$ K. The partial pressure of CO_2, used as an inactive gas, at 139 K is 1 Torr.[6]

Nanostructured films were obtained in low-temperature cryostats described previously.[2] The specimens were formed by the vacuum deposition of lead and carbon dioxide vapours onto a support with Ni/Cr comb-shaped electrodes for conductivity measurements; the support was attached to a copper cryogenic unit cooled with liquid nitrogen. The specimens were studied by scanning tunnelling microscopy and FTIR spectroscopy; furthermore, the electric conductivity of the films was measured as a function of humidity and exposure to 1% ammonia vapours.

Metal condensates usually display the most interesting electrophysical properties near the percolation threshold since the specimens are non-conducting below this threshold, whereas at much higher temperatures they become continuous conductive metallic films. The metal deposition was continued until the conductivity started to increase, which occurred at surface resistances of the specimens around 10^9 Ω cm^{-2}. According to calibration data, the condensation rate of lead at 700 °C was 2.5×10^{-9} mol h^{-1}, whereas that of CO_2 was 5.33×10^{-7} mol h^{-1}. The condensation times of the reagent vapours were 10 and 50 min.

It is well known that metals react with carbon dioxide at low temperatures to give various complexes.[7] Cryococondensates with various Pb:CO_2 ratios were studied by IR spectroscopy at 80–300 K. Figure 1 shows the IR spectra of the test samples.

The assignment of absorption bands in the spectra was based on published data[7] and an IR spectrum of solid CO_2 at 80 K. The IR spectrum of lead–carbon dioxide cocondensates contains two intense bands at 2364 and 2339 cm^{-1}, which correspond to the asymmetric vibrations of carbon dioxide, and a weak band at 1399 cm^{-1}, which corresponds to the symmetric vibrations of CO_2. Similar absorption bands are also present in the spectrum of solid carbon dioxide (Figure 1, spectrum *2*). Thus, IR-spectroscopic data showed no interaction of lead with carbon dioxide at 80–300 K.

The relief of film surfaces was studied by scanning tunnelling microscopy (STM). The maximum scanning area was 5×5 μm.

An image of the surface area for a film obtained by cryococondensation of lead and carbon dioxide vapours and the results of statistical analysis of particle size distribution, are presented in Figures 2 and 3. One can see that the morphology of cocondensate films depends considerably on the component ratio during the film formation. 'Gaps' with a mean depth of 20 nm appear; we believe that they are formed due to the sublimation of carbon dioxide from the cocondensate. A comparison of our images with micrographs obtained in the absence of carbon dioxide[8] shows that the presence of CO_2 in the cocondensate affects lead particle size and film surface morphology.

Statistical analysis of STM profiles showed that the mean size of particles with an excess of carbon dioxide or lead was 33 or 13 nm, respectively. We believe that, in an excess of lead, the majority of particles are formed in the flow before interaction with the cold surface. The fraction of surface atoms,

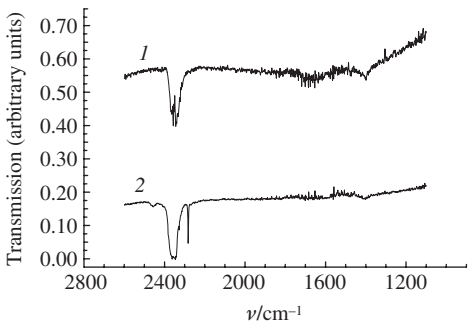

Figure 1 IR spectra of cryococondensates at 80 K: (*1*) lead–carbon dioxide; (*2*) carbon dioxide.

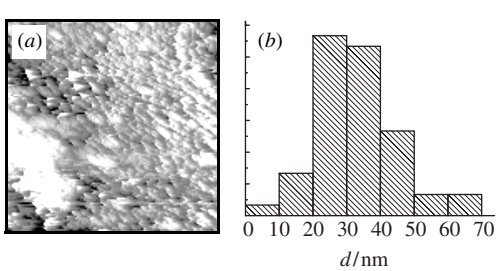

Figure 2 (*a*) STM micrograph and (*b*) particle size distribution bar graph of a nanostructured thin film with excess carbon dioxide after annealing to room temperature. The scanning area is 1.6×1.6 μm. The mean particle size is ~33 nm. The Pb:CO_2 ratio is 1:3.

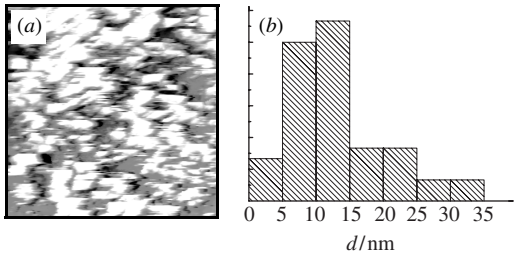

Figure 3 (*a*) STM micrograph and (*b*) particle size distribution bar graph of nanostructured thin films containing excess lead after annealing to room temperature. The scanning area is 0.27×0.27 μm. The mean particle size is ~13 nm. The Pb:CO_2 ratio is 1.4:1.

the effective adsorptive activity and hence the contribution of the surface to electrophysical properties is greater in smaller particles than in larger specimens. Thus, the results of scanning probe microscopy showed that the use of carbon dioxide as a low-temperature matrix affects the particle size and the surface properties of metallic lead films.

Chemoresistive properties with respect to ammonia and humidity were determined. The measurements were carried out in a chamber that allowed us to change the relative humidity from 5 to 95%. The humidity probe built-in in the chamber was connected to a Keithley 6517A electrometer, which allowed us to measure the film resistance and relative humidity simultaneously. In experiments with ammonia, the concentration of humid ammonia amounted to 1%.

The cocondensates of Pb and CO_2 vapours were heated to room temperature; air was let in, and resistance was studied at various relative humidities. Figure 4 shows the dependence of the specimen conductivity on relative humidity at various reagent ratios.

It was found that, after CO_2 sublimation, a change in the relative humidity from 5 to 95% results in an increase in the conductivity by two or three orders of magnitude. The film sensitivity was measured as a ratio of a current at 95% air humidity ($I_{95\%}$) to a current through the film in dry air ($I_{5\%}$): $S = I_{95\%}/I_{5\%}$ at a constant voltage of 10 V. The mean values determined in this way were $S = 1379$ for condensates with Pb:CO_2 = 1:3 and $S = 2388$ for condensates with Pb:CO_2 = 1.4:1.

The film resistance nonlinearly changes with humidity. The specimens with the smallest mean particle size have the largest sensitivity to humidity.

The resistance of the specimens varied similarly to that of lead films synthesised without carbon dioxide.[5] Thus, films prepared by various methods show a similar adsorption response of electric conductivity to changes in the relative humidity.

Figure 5 shows the variation in the conductivity of lead–carbon dioxide cryococondensates with time.

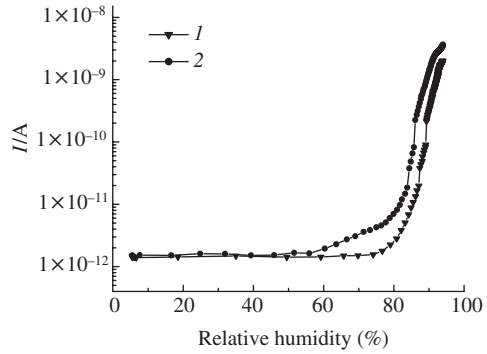

Figure 4 Dependence of the specimen conductivity on relative humidity (*1*) Pb:CO_2, 1:3; (*2*) Pb:CO_2, 1.4:1.

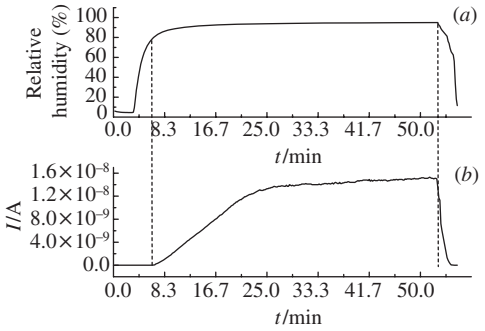

Figure 5 Variations in (*a*) relative humidity and (*b*) response of specimen conductivity.

It was found that the sensor response time amounts to a few minutes. For island films, it is shorter than 10 s.[8] Thus, the response time is smaller for thinner films. The observed changes in the conductivity were reversible: the film conductivity returned to the original value after water removal. The resistance of the specimens increases by one order if 1% aqueous ammonia is used. The practical use of the material for ammonia determination is hindered by the sensitivity to water vapour. This problem can be solved by creating mixtures with a constant humidity or by independent humidity measurements.

We believe that the increase in the sensitivity of specimens obtained by the low-temperature vacuum cocondensation of lead and carbon dioxide vapours primarily results from an increase in the total number of adsorption centres due to an increase in the adsorbent surface area and the formation of a finer surface microrelief.

After a specimen withdrawn from the cryostat contacts air, a thin film of lead oxide is formed on the surfaces of the lead particles.[9] This oxide layer causes lead films to have chemoresistive properties. In such a case, the response mechanism is probably similar to that generally accepted for metal-oxide semiconducting sensors and results from the formation of a charged form of chemisorbed oxygen.[10] Adsorption of gas molecules capable of changing the concentration of charged surface particles due to competition for adsorption centres can change the surface charge, which affects the specimen conductivity. The materials studied in this work differ from metal oxide films in that the nanoparticles have only thin oxide semiconducting shells that coat the metal core. The metal can serve as an electron donor, thus increasing the concentration of the charge carriers in the oxide surface layer.

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