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Self-Assembled Cu/Cu_2O Multilayers: Deposition, Structure and Optical Properties

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ABSTRACT

The structure of Cu/Cu_2O multilayers fabricated by nonlinear electrochemical deposition has been tuned in two ways: electrochemically, by alteration of the deposition current, and by in-situ illumination during deposition. By choosing the current the thickness of the layers can be controlled, and by choosing the illumination power density the size of the particles forming the copper composite layer can be controlled. These lead to significant changes of linear and nonlinear optical properties of Cu/Cu_2O multilayers.

New nanoscale materials that are of great importance to the rapidly developing field of nanoelectronics can be fabricated by means of an electrochemical technique. Electrodeposition under conditions of spontaneous voltage oscillations gives multilayered structures in a simple and inexpensive way.[1] Changing the electrodeposition parameters results in a change of the thickness of alternating layers as well as the layer composition, that leads to a change of the physical properties of the whole structure. On initial stages of nonlinear electrodeposition, nuclei are formed on the surface followed by particle growth. This gives a nanoscale material with the reduction of dimension in two ways: nanometer-size layers (2-D structure) consist themselves of nanoparticles (1-D structure).

Although spontaneous oscillations in electrochemical processes are rather common, the only multilayered structure reported to be fabricated in this way is the Cu/Cu_2O structure.[1−3] Materials composing this structure by themselves reveal rather interesting properties that can be utilized in optoelectronic devices. Cuprous oxide is a p-type semiconductor with strong excitonic properties, existing up to room temperature. Excitonic excitation can be localized in a confined space of a nanoparticle and then be transformed back into light: this idea of a nanoaperture has been suggested in ref 4. The presence of metal nanoparticles leads to the enhancement of an electromagnetic field inside and/or around the particle that can make solid−light interaction even more effective.

Linear optical properties and the layer composition in Cu/Cu_2O multilayered structures fabricated with different electrodeposition conditions have been studied in ref 1. Periodicity of the structures has been confirmed there by TEM. A thicker layer formed at more negative voltage in the oscillation is a Cu/Cu_2O composite, with the copper concentration being dependent on current density. A thinner layer formed at more positive voltage is cuprous oxide. The composite layer consists of particles of tenths of nanometers, but the composition of the particles and the dependence of optical properties on a particle size is not clear. Voltage oscillations appear only in specific conditions. If the current is chosen, the thickness and composition of the layers might be controlled in an electrochemical way (for instance, by changing pH or temperature), but the range of such tuning is rather small. To our knowledge, there is no evidence of the dependence of particle size on deposition current.

To make a structure with properties tunable in a wider range, it is necessary to look for alternative possibilities for affecting the structure by the use of nonelectrochemical interactions. The change of the particle size has been reported in Cu/Cu_2O multilayers electrodeposited in a magnetic field:[5] the size of the particles increased up to 1 μm magnetic field of 5 T.

In this paper we report the results of the studies of the influence of electrodeposition current density on the structure and optical properties of Cu/Cu_2O multilayers. Reflectivity and second harmonic generation (SHG) were studied. Optical tuning of the particle size has been performed and the resulting change of optical properties has been studied.

The nonlinear electrodeposition technique, which uses spontaneous voltage oscillations, is described in refs 1−3.

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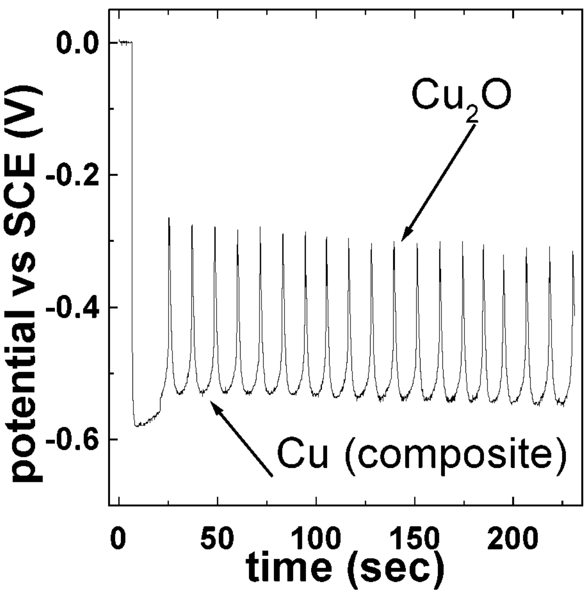

Figure 1. Voltage oscillations for the current density 1 mA/cm^2. Interruption of the process at the bottom and top of oscillations gives a composite and cuprous oxide upper layer, respectively.

Table 1: Structural Parameters of Cu/Cu_2O Multilayers

I mA/cm^2	d^{comp} nm	d^{ox} nm	$d^{comp,a}$ nm	$d^{ox,a}$ nm	$p^{cu,a}$
0.25	6.5	0.6	5	0.4	0.11
0.5	8.0	1.3	6	0.7	0.53
1	13.4	1.7	11	1.4	0.56
2	25.9	3.5	20	2.5	0.77

[a] The thickness of the layers is taken from ref 1.

In our experiments the deposition solution contained 3 M of lactic acid and 0.6 M of copper(II) sulfate pentahydrate. The pH of the solution was varied in the range of 8.5 to 10. The deposition current was varied from 0.25 mA/cm^2 to 2 mA/cm^2. Figure 1 shows the time dependence of voltage oscillations for the current density $i = 1$ mA/cm^2. We started with the single oscillation (number of deposited layers $N = 1$) up to 50 oscillations ($N = 50$). We estimated the thickness of the layers using Faraday's law, with the copper concentration taken from ref 1 for the same experimental conditions. These data are presented in Table 1 (there d^{comp} and d^{ox} are the composite and oxide layer thickness respectively, p^{cu} is the copper concentration in the composite layer). A deposition process can be interrupted on different stages: on bottom (−0.55 V) or on top (−0.3 V) of voltage oscillations, then the upper layer is composite or cuprous oxide, respectively.

The topography of multilayers was studied by AFM (using Nanoscope III, Digital Instruments). The AFM image of the Cu/Cu_2O structure with the composite on top is shown in Figure 2a. AFM micrographs demonstrate that the individual layer consists of the particles with in-plane size of 20−30 nm in diameter. Nanoparticles form aggregates of average size about 200−300 nm. The AFM image taken with the cuprous oxide upper layer does not reveal any difference from the presented one. We did not find any changes of lateral particle size when the current density was changed, except of the initial stage of the deposition process. Before

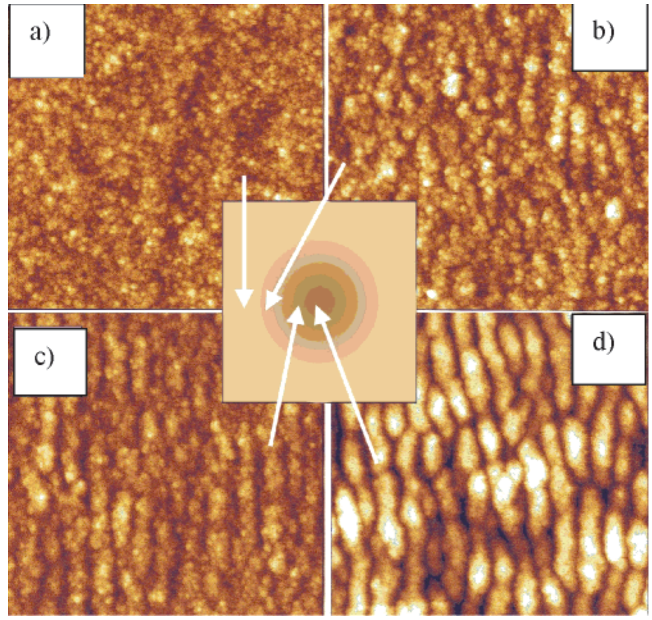

Figure 2. (a) AFM image of Cu/Cu_2O multilayers with $N = 20$, $I = 1$ mA/cm^2, cuprous oxide layer on top. (b)−(d) AFM images for the sample illuminated by Argon laser during deposition process in the different points of illuminated spot that are indicated by arrows. The size of the images is $3\mu \times 3\mu$.

the first oscillation starts, the particle size in the deposited (i.e., composite) layer is smaller, down to 10−15 nm. As the estimated thickness of the layers is smaller than the lateral particle diameter, the particles should be considered as prolate spheroids with rather high values of eccentricity.

Reflectance spectra of multilayers and copper substrate (polished and kept in air) in the range of 1.5 to 3 eV are presented in Figure 3. Polarization of incident (α-in, α = p,s: in-plane and perpendicular to the plane of incidence) and reflected (β-out) was controlled by Glan prisms. The reflectance spectrum of the substrate (see Figure 3a) corresponds to the spectral dependence of the dielectric constant of a bulk copper.[6] For multilayers, the reflectivity spectrum in p-in, p-out polarization combination reveals a strong minimum around 2.2 eV and a shoulder around 1.8 eV. For the s-in, s-out polarization combination, only minima around 2.2 eV are left for all samples. The change of reflectivity spectrum of nanostructures in comparison to the bulk copper arises due to several reasons. If the absorption in the layer is not very high, the main change is due to an interference effect in the thin layer. This effect is dominant, for instance, in thin films of oxidized copper particles.[7] If the absorption is high, then the thickness of the layer does not play a significant role, as electromagnetic waves do not penetrate deeply into the film and optical properties are determined by the outer layers of the structure. In this case the observed minimum should be attributed to the properties of a single particle. The change of deposition current leads to the change of the total thickness of the structure and refractive index (due to copper concentration change) as well. Both reasons can cause the shift of minimum in the measured reflectivity spectra. No specific features that can be attributed to the cuprous oxide have been found.

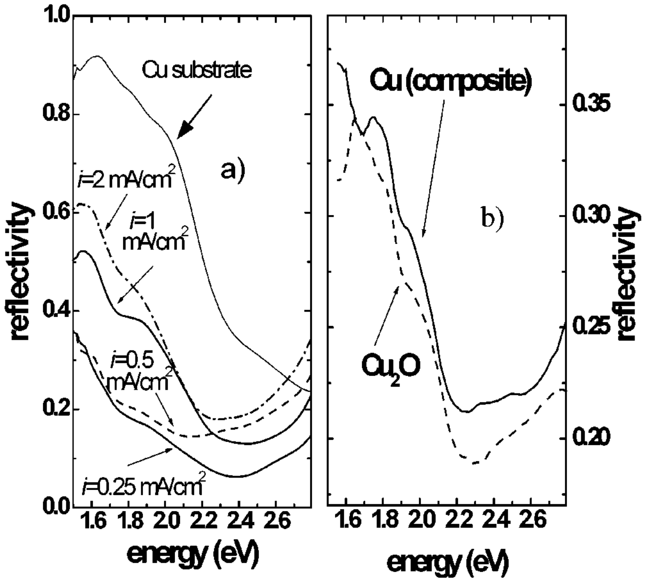

Figure 3. (a) Reflectance spectra of Cu/Cu_2O multilayers deposited with different current density: number of layers $N = 20$. (b) Reflectance spectra from the structures with the deposition process stopped at the bottom (composite, $N = 20$) and the top (cuprous oxide, $N = 20.5$) of voltage oscillations. Polarization combination is p-in, p-out.

We compare the reflectivity of the samples with composite and cuprous oxide on top in two ways. First of all, we study reflectivity (far field) in a way described in the previous paragraph. The examples of reflectivity spectra measured for two samples with $N = 20$ (copper composite on top) and $N = 20.5$ (cuprous oxide on top) are shown in Figure 3b. The shape of the spectrum remains the same, but the value of reflectivity is reduced by 5% for cuprous oxide top layer.

In addition, we studied near-field reflectivity using SNOM (spatial resolution of about 100 nm). The SNOM images in an optical mode for two samples with cuprous oxide and copper composite on top are shown in Figure 4, respectively. The contrast of the local reflectivity for these two samples is much higher than the contrast of the total reflectivity. This may be due to the averaging of the optical signal in far-field reflectivity measurements over a much bigger area that is not homogeneous. However, both data confirm, in respect to linear optical properties, the presence of two distinctively different layers repeated periodically in the whole structure. Presented SNOM images in the optical mode as well as ones in the topographic mode show particle aggregates of about 300 nm, of the same size that was observed in AFM.

For the SHG studies, a fundamental radiation from a Q-switched Nd:YAG laser (Coherent Infinity 40−100) was used at wavelength $\lambda_\omega = 1064$ nm, pulse width 3.5 ns, repetition rate 50 Hz, and energy 0.2 mJ/pulse. The fundamental beam was focused on the sample surface at a 45° angle of incidence to a spot of ~0.5 mm diameter. Polarization of the fundamental and SHG waves was controlled by Glan prisms and remained in the plane of incidence. SHG signal was discriminated spectroscopically by appropriate color and interference filters and directed into a PMT (Hamamatsu, R7400U-02). The signal from the PMT was processed by a boxcar average integrator (Stanford Research SR245). SHG from the YAG laser system was also used for measurements of local reflectivity. Figure 5a shows the SHG intensity dependence on the deposition current. In this dependence, the increase of the current causes the increase of the SHG intensity. However, if the structures with the same thicknesses as for the samples shown in Figure 5a by solid line are deposited with the equal current, the SHG intensity dependence on the thickness is less sharp (dashed line). This means that the increase of the SHG intensity with the change of current density is caused rather by the change of structure and composition than the increase in thickness. The SHG intensity from the samples with composite and cuprous oxide top layers is shown in Figure 5b. The SHG signal is higher in the case of the composite top layer for any number of layers. It means that, with respect to nonlinear optical properties, the structure is periodic.

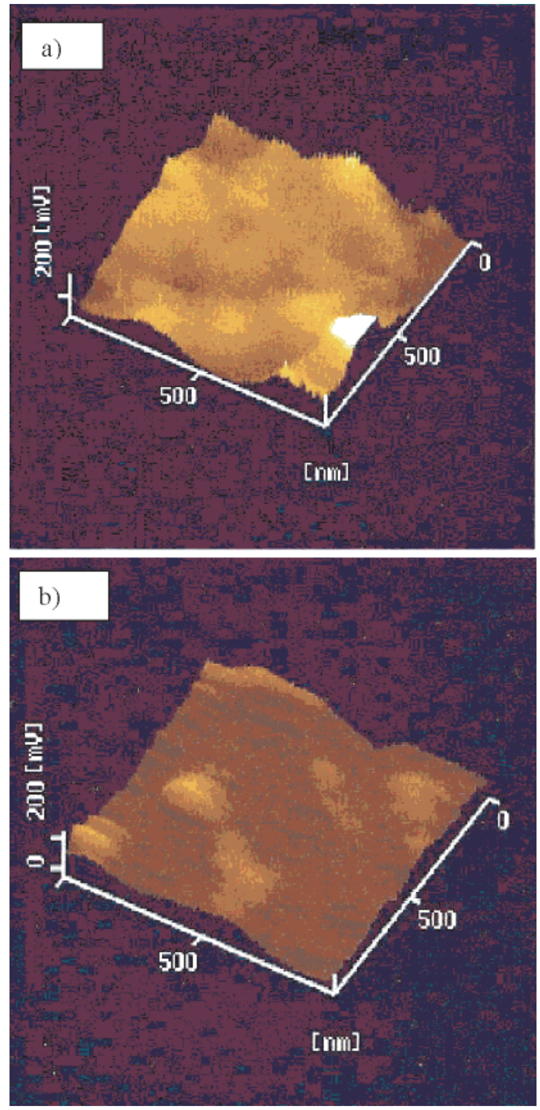

Figure 4. SNOM images of the Cu/Cu_2O multilayers with the top copper composite layer (a) and cuprous oxide layer (b). The sensitivity is the same for both images.

For tuning the particle size in the layers, illumination of the structure during fabrication has been performed. The output of the CW Ar laser was used for in situ illumination with the power of 200 mW focused onto a spot of 3 mm in

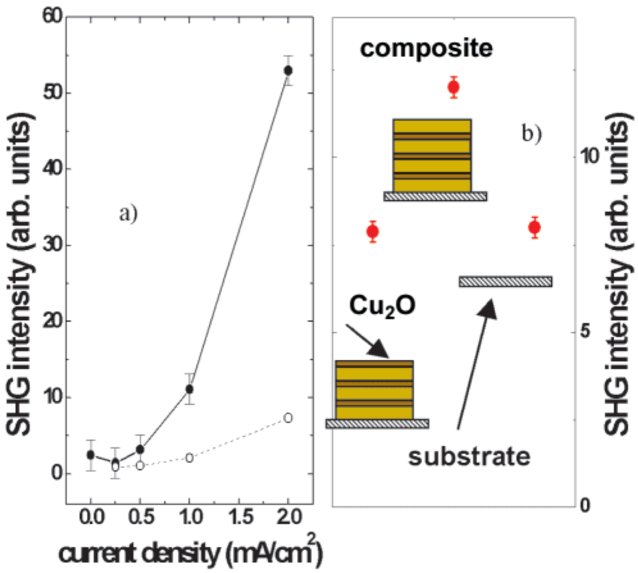

Figure 5. (a) SHG intensity dependence on the deposition current (filled circles) and the same dependence, reconstructed from the measurements for the samples with different number of layers (different thickness), deposited with $i = 1$ mA/cm^2; (b) SHG intensity at 532 nm for the same samples as in Figure 3b.

diameter. Figure 2 shows the AFM images of the structure in the different points of the laser spot. The AFM tip was moved along the illuminated area from outside the laser spot (Figure 2a) to the center (Figure 2d) through the intermediate points (Figures 2c and 2d). The changes of the structure, i.e., the increase of the particle size and change of shape and orientation, depend on the tip position in respect to the illuminated spot. As the laser beam is Gaussian, the laser power density is maximal in the center. There could be two possible mechanisms of the influence of the laser light on the structure formation. The first one is due to the photoinduced effects; the second one is due to the heating. Both effects can be dependent on the power density, but as the fundamental energy falls beyond the band gap, on one hand, and the deposition process is sensitive to thermal conditions,[8] the heating of the substrate looks like a more probable reason for the structural changes during deposition. Orientation of the particles arises due to the inhomogeneity of the heating: the long axis of the cigar-like particle is oriented perpendicular to the temperature gradient. Probably the single particle is formed along the iso-thermal line.

Local reflectivity along the illuminated spot was studied using YAG laser system at 532 nm, the cross-section is shown in Figure 6 by a solid line. For the same positions of the laser beam, the SHG was measured (Figure 6, dashed line). The higher the local power density of illuminated area, the more the increase of reflectivity and the decrease of the SHG intensity.

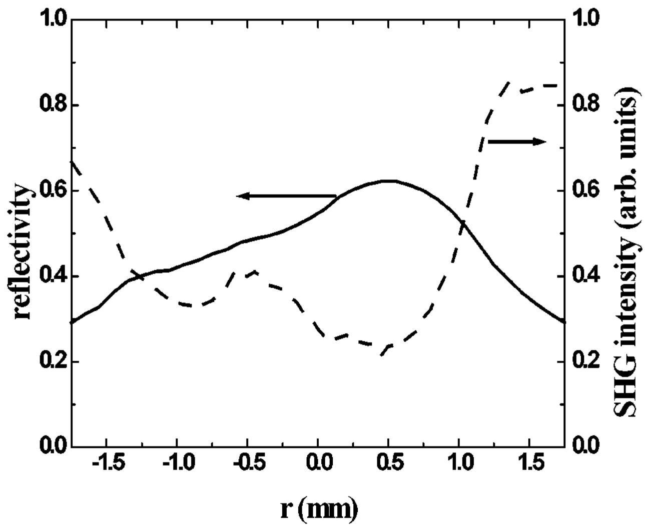

Figure 6. Reflectivity (solid line, left scale) and SHG intensity (dashed line, right scale) dependences on the position of the probe laser beam measured from the center of the illuminated spot: the probe beam diameter is 0.5 mm.

In conclusion, the Cu/Cu_2O multilayers with altering structure and optical properties have been fabricated by spontaneous voltage oscillations during electrodeposition. We proved by optical measurements that the layered structure of electrodeposited composites, as both reflectivity and SHG intensity, varies periodically. In addition to an electrochemical way of changing the structure and therefore the properties of multilayers, we found an optical one. It allows us to tune the shape of the particles within the layer that leads to variation of the optical properties in a wide range.

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