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Low temperature formation Silver-Copper alloy nanoparticles using hydrogen plasma treatment for fabrication of humidity sensor

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ABSTRACT

In this paper, a novel method of producing bi-metallic alloy nanoparticles at low temperatures using hydrogen bombardment of thin films, deposited on glass substrates, is introduced. Optical and morphological characteristics of the nanoparticles were extensively studied for various conditions of plasma treatment, such as plasma power density, temperature, duration of hydrogen bombardment, thickness of the initial thin metallic film etc. As an important application of fabricated alloy nanoparticles, humidity sensor based on the alloy nanoparticles was introduced. It was shown that Ag-Cu alloy nanoparticles ionizing ability of the fabricated alloy nanoparticle is higher than Ag and Cu nanoparticles. Scanning Electron Microscopy, Atomic Force Microscopy and Transmission Electron Microscopy were used to analyze the nanostructures.

Keywords: *Nanoparticles; Plasma; Hydrogen; PECVD; Humidity sensor Ag-Cu; Alloy.*

INTRODUCTION

Because of their linear and nonlinear optical properties, metal nanoparticles have been widely studied in recent years. They are suitable candidates for various devices because of their unique optical [1], electronic [2], catalysis [3], chemical [4] properties. Many different methods were applied for producing nanoparticles such as chemical synthesis [5], exploding wire [6], and laser ablation [7]. We have used a novel different method that produces nanoparticles at a temperature much lower than the melting point of their respective bulk using hydrogen plasma in Enhanced Chemical Vapor Deposition system. In this work, bimetallic alloy of silver-copper nanoparticles were produced by this plasma treatment method.

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This method can also be used for the formation of other metallic or semiconductors nanoparticles by PVD method on glass or silicon or other substrates, out of which two examples of nickel and silicon nanoparticles are presented.

Optical properties of metal nanoparticles are related to the excitation of surface Plasmon. The parameters such as size and shape [8, 9], surrounding medium [10], metallic species [11] of nanoparticles change the excitation energy of surface plasmons. We have investigated the optical behavior of nanoparticles as a function of structural parameters.

Finally, ionizing ability of Ag-Cu alloy nanoparticles was compared with that of the pure Ag and Cu nanoparticles. It was shown that the alloy Ag-Cu nanoparticles can be a promising candidate for fabrication of humidity sensor.

EXPERIMENTAL

The work started by cleaning the glass substrate in the standard RCA#1 solution , which contained $NH_3/H_2O_2/DI\text{-}H_2O$ with relative volume proportions of 1:1:5, and followed by the deposition of a thin layer of Ag-Cu with the thickness of about 10 nm in a thermal evaporation system at the base pressure of 5×10^{-6} torr. [Ag and Cu were evaporated simultaneously in two separated crucibles]. The coated glass was then put in the direct current plasma enhanced chemical vapor deposition (DC-PECVD) apparatus, as shown schematically in Figure 1. This DC-PECVD setup has two flat electrodes which hydrogen plasma forms between them by the application of a voltage between the electrodes. The sample was placed on the cathode (lower electrode) and during the plasma treatment was bombarded by hydrogen radicals. We made an electrical connection between the metallic layer and the cathode to prevent the build up of positive charges on glass substrate that might repel the plasma. The substrate temperature was varied between 200 and 400 °C and the hydrogen pressure was maintained at 0.4-2 torr during the Plasma treatment in the DC-PECVD system. The flow rate of hydrogen was kept between 50 to 70 Sccm. The power density of the DC-PECVD reactor during the hydrogen bombardment step was varied between 100 and 800 mW/cm^2. The subsequent annealing step was conducted *in situ* at a substrate temperature of 50 °C higher than what had been used for the bombardment step. These successive plasma treatment/annealing steps were carried out for each sample. Based on the investigation conducted in this study, the bombardment step served to etch the deposited layer, forming nano-clusters and nucleation sites for subsequent formation of the nanoparticles. However, it was observed that if the duration of the hydrogen bombardment step exceeded a certain time, the entire deposited layer was removed. During the annealing period, the hydrogen trapped in the layer was ejected out and some energy was imparted to the nano-structures, enhancing the chance of formation of the nanoparticles. It should be mentioned that this step has been performed in the absence of hydrogen plasma. On the other hand, it has been observed that if the annealing step is carried out for longer periods, the small grains of nanoparticles merge, forming larger grains. The sequence of consecutive hydrogen bombardment and annealing steps has been found to be an optimal condition for the evolution of nanoparticles.

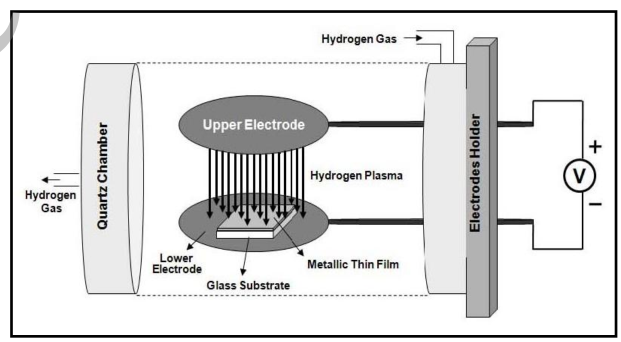

Fig. 1. Schematic diagram of DC-PECVD chamber showing two electrodes being connected to a voltage supplier. The rest of the apparatus including the heater, the temperature control, the inlets and the outlets etc are not shown.

Duration and temperature of annealing and bombardment steps, plasma power, and the thickness of the initial thin metallic film influence the size of nanoparticles. We have investigated the effects of such parameters on nanoparticles size and the absorption spectra. Scanning electron microscope and atomic force

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microscope were used to analyze the surface morphology of the as-prepared samples.

For analyzing the humidity sensing behavior of the fabricated alloy nanostructures a 200nm thickness of gold layer was deposited on the structure using a sputtering system at a base pressure of 2×10^{-6} torr. Then by using a standard photolithography two electrodes were patterned. Prepared samples were then soaked in water and by applying the voltage between the electrodes ion current was flown between the electrodes and it was measured.

RESULTS AND DISCUSSION

Figure 2 includes four atomic force microscope (AFM) and two scanning electron microscope (SEM) images of as-prepared silver and silver-copper nanoparticles demonstrating surface morphology and nanostructures of the samples prepared at different condition of nanoparticles formation. As shown in this figure well-isolated nanoparticles with different diameter size were obtained. The preparation condition and the final average size of each sample are given in Table 1. The thickness of the initial layer for Ag samples (a-d) was about 10 nm and for Ag/Cu alloy samples (e & f) was about 16 nm, which contained 70% Cu and 30% Ag by weight.

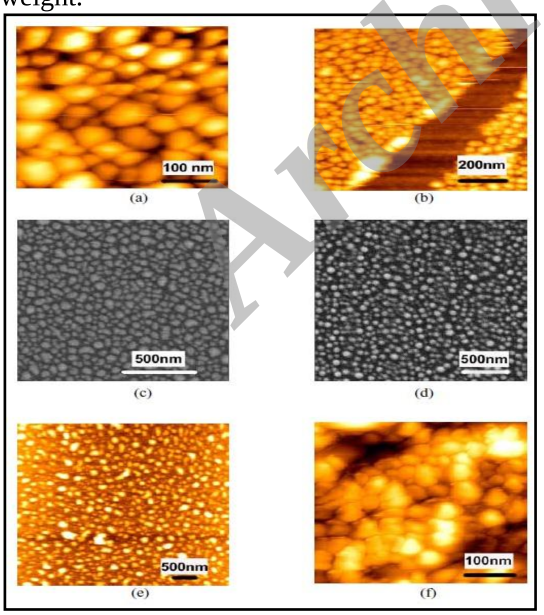

Fig. 2. AFM and SEM images of silver nanoparticles (a-d) and Ag/Cu alloy samples (e & f) formed on glass substrates using hydrogen plasma treatment, showing that different conditions of sample preparation lead to different sizes of nanoparticles.

Table 1. Sample preparation conditions for Figure 2

Average Particle Size (nm)	Plasma Power Density mW/cm²	Bombardment Condition		Sample
		Temperature °C	Duration minutes	
75	200	300	15	A
50	180	300	20	B
65	230	300	20	*c
70	300	380	20	D
145	120	220	20	E
55	130	300	15	F

* It was then annealed at 400 °C for 20 minutes.

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For investigating the optical properties of bimetallic nanoparticles we have prepared two samples with different conditions of plasma treatments. Figure 3 shows the absorption spectra of two Ag/Cu nanoparticles prepared at two different temperatures of 200 and 300 ºC during the bombardment step. As shown in this figure, the sample prepared at the lower temperature has two isolated peaks corresponding to the absorption peaks of pure silver and pure copper nanoparticles whilst the other one (dashed curve) has a single peak at a wavelength between the two above-mentioned peaks. It depicts that the sample with two peaks is just a mixture of Ag nanoparticles and Cu nanoparticles but the other one is an alloy of Ag/Cu nanoparticles.

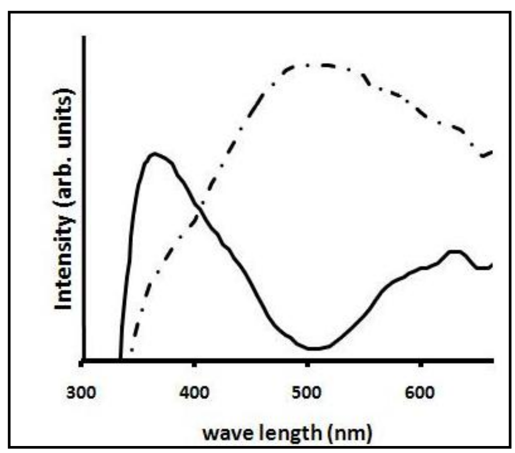

Fig. 3. Absorption spectra of samples that having different temperature in their bombardment steps. The sample that exhibits two peaks in its absorption spectrum, bombarded at 200 °C, shows the formation of separated Ag and Cu nanoparticles, not alloy. The other sample, which is bombarded at 300 °C, shows one peak in its spectrum that can be attributed to alloy formation.

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Figure 4 shows the absorption spectra of Ag and the alloy nanoparticles with different mixing ratio. As shown in this figure, shifting the absorption peak towards the blue or red regions depends on the mass percentage of silver or copper components in the alloy. TEM analysis of as prepared alloy nanoparticles was shown in the Figure 5 demonstrating the formation of alloy nanoparticles. By looking carefully at this image, one can see that some parts of some grains in the TEM image are darker, which means that these grains contain the two component materials and thus the alloy of silver/copper was formed in this sample.

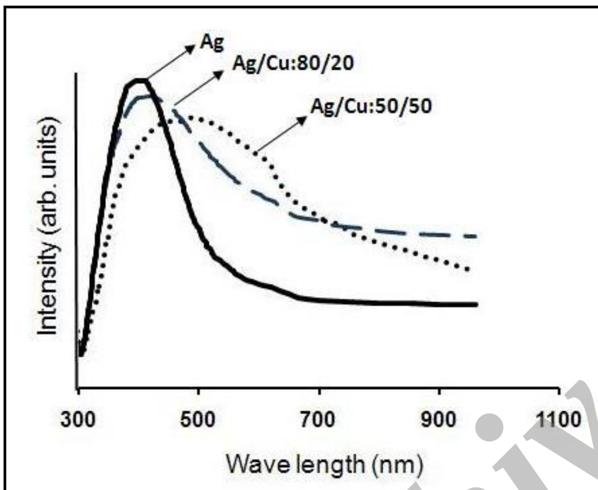

Fig. 4. Comparison between absorption spectra of Ag/Cu alloy nanoparticles with different weight ratio of Cu that have been prepared at the same condition. It shows that increasing the Cu ratio in particles shifts the absorption spectrum towards the absorption spectrum of pure Cu nanoparticles.

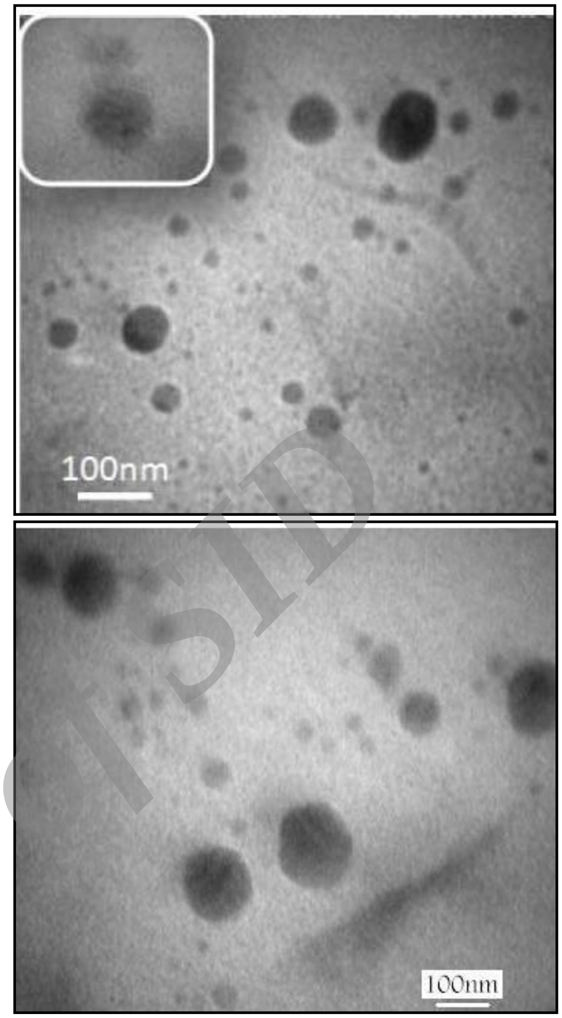

Fig. 5. TEM images of silver/copper alloy nanoparticles showing that the grains were formed by this method. The darker color of some parts of the grains shows that the grains contain more than one material, and thus the silver/copper alloy nanoparticles were formed.

Electrical characteristics of the as prepared nanoparticles in water were represented in Figure 6 to show ionizing ability of the nanoparticles. This figure represents I-V characteristics of the pure Ag and Cu and alloy Ag-Cu nanoparticles. As shown in this figure ionization current obtained by alloy nanoparticles at a same applied voltage is higher than pure Ag and Cu nanoparticles. It seems that the enhanced ionizing behavior of alloy nanoparticles is because of the high electrical conductivity of Cu. It is obtained from this result that Ag-Cu alloy nanoparticles are a promising candidate for fabrication of humidity sensors.

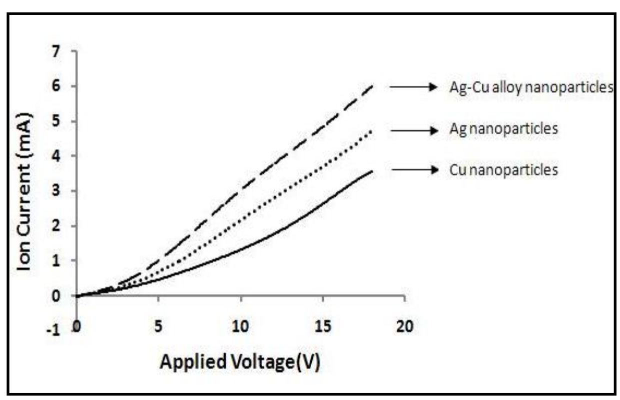

Fig. 6. I-V characteristics of the pure Ag and Cu and alloy Ag-Cu nanoparticles. The alloy nanoparticles have a high ion current comparing with the pure Ag and Cu nanoparticles.

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CONCLUSIONS

In summary, we have successfully produced the silver-copper alloy nanoparticles using a low temperature plasma bombardment method, well below the melting point of the sample constituents. The method can be used for any other materials to produce nanoparticles of them on any arbitrary substrates (even flexible substrates). It is easy to make a patterned structure of nanoparticles by this method. Optical measurements of as-prepared nanoparticles confirm the quantum behavior of the samples arising from decreasing the size and confinement. Ionizing ability of as prepared alloy nanoparticles was measured and compared with the pure nanoparticles. Alloy nanoparticles were introduced as a promising material for humidity sensing applications.

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