

Low-Temperature Raman Spectroscopy of Copper and Silver Nanoparticles Ion-Synthesized in a Silica Glass and Subjected to Laser Annealing

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Abstract—The modification of the shape of ion-synthesized silver and copper nanoparticles in a silica glass during laser annealing has been studied for the first time by Raman spectroscopy at a temperature of 77 K. The laser annealing has been carried out for a wavelength of 694 nm at the edge of the plasmon absorption spectrum of nanoparticles. A comparison of the experimental spectra and the calculated modes of in-phase bending vibrations of the “harmonica” type in nanostrings of the corresponding metals has demonstrated their good agreement. The effects observed have been discussed from the standpoint of the size quantization of vibrations in metal nanowires. This methodical approach has allowed us to estimate the sizes of the Ag and Cu nanoparticles under the assumption that they have an elongated form; in this case, their average lengths are equal to 2.5 and 1.4 nm, respectively.

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1. INTRODUCTION

At present, nanocrystalline materials have attracted particular attention from the viewpoint of both their practice application and fundamental research. Significant progress has been reached in studying the size quantization of semiconductor nanocrystals [1]. However, as regards metal nanoparticles, the lack of experimental data leads to an incomplete understanding of the nature and specific features of quantum-size effects and related optical phenomena [2]. In this respect, the aim of this work is to synthesize noble metal nanoparticles dispersed in a dielectric matrix (SiO₂) and to study them by low-temperature Raman spectroscopy. Previously, in the Raman scattering spectrum of silica glass containing spherical silver and copper nanoparticles, the low-frequency peaks [3–7] were revealed at room temperature, and they were attributed to the excitation of acoustic vibrations in metal nanoparticles. It was also shown that the Raman shift corresponding to the frequency of these vibrations is dependent on the nanoparticle size. Therefore, it can be expected that Raman spectroscopy will allow one to trace variations in the sizes and the shape of ion-synthesized metal nanoparticles in glasses after the action of high-power laser pulses on them [8]. The control of metal nanoparticle sizes is important for optimizing the operation of non-linear-optical [9] and sensor [10] devices fabricated using nanostructured materials.

It should be noted that processes of formation and modification of metal nanoparticles have been also extensively studied using other optical methods (e.g., reflection and transmission spectroscopy) [2, 11, 12], as well as atomic-force microscopy [13]. In some works [14, 15], the modification of metal nanoparticles in various dielectrics was carried out using high-power pulses of excimer lasers. These studies showed that this laser irradiation results in a decrease in the size of spherical nanoparticles. As follows from the literature review presented in [8], glasses containing copper and silver nanoparticles were not previously annealed by ruby lasers ($\lambda = 694$ nm). Therefore, in this work, we studied Raman scattering by silver and copper nanoparticles in silica glasses exposed to nanosecond laser pulses. The Raman spectra obtained were used to estimate the degree of modification of sizes and shape of metal nanoparticles.

2. SAMPLE PREPARATION AND EXPERIMENTAL TECHNIQUE

Copper and silver nanoparticles were synthesized in a SiO₂ matrix (silica glass) by implantation of Cu⁺ and Ag⁺ ions with energies of 160 and 60 keV, respectively. In both cases, the ion dose was 5×10^{16} ions/cm² at a current density of 10 μ A/cm² in the ion beam. The ion implantation was carried out at room temperature of the irradiated glasses. The optical transmission

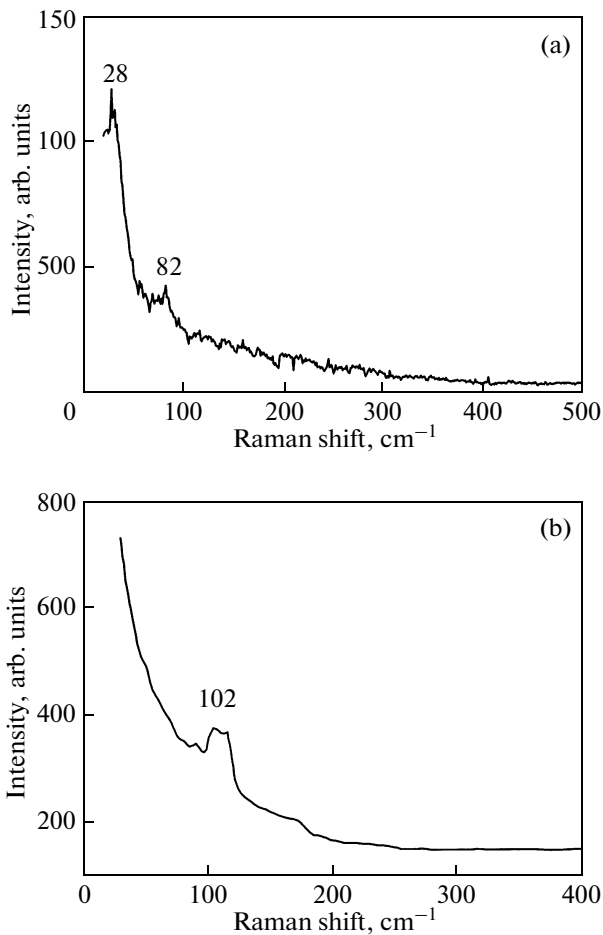


Fig. 1. Raman spectra measured at 77 K for (a) SiO₂ with silver nanoparticles and (b) SiO₂ with copper nanoparticles.

spectra were measured on a Hitachi-330 two-beam spectrophotometer in the range 350–900 nm. The optical transparency of the substrates before implantation in the visible spectral range was ~90%.

Laser annealing of ion-synthesized layers was performed by single pulses of a ruby laser in the transparency region of the glass at the wavelength $\lambda = 694$ nm for the pulse durations $\tau_i = 75$ and 50 ns with energy densities per pulse $W = 0.85$ – 1.4 J/cm².

The Raman scattering in composite materials was excited by an LGN-502 ($\lambda = 488$) continuous wave argon laser with a power of 100 mW. The spectra were measured at temperatures of 300 and 77 K in the reflection geometry on a DFS-52 spectrometer in the photon counting mode with a scan step of 1 cm⁻¹ and the accumulation per point for 30 s.

3. RESULTS AND DISCUSSION

As was shown in the review [8], the aforementioned implantation conditions (ion energy, doses, and substrate temperatures) result in the formation of spheri-

cal metal particles in the near-surface layer of a silicate glass. The formation of the noble-metal nanoparticles in the case under consideration is confirmed by appearance in the optical transmission spectra of wide single bands due to the effect of the surface plasmon absorption with maxima in the range 590–600 nm in the case of copper nanoparticles (in a Cu : SiO₂ sample) and near 450 nm for silver nanoparticles (in an Ag : SiO₂ sample) [2]. At the same time, the low-frequency Raman scattering spectra of these samples measured at room temperature have no any weak peaks related to spherical metal nanoparticles expected from the available literature data. A possible explanation of the absence of the peaks is a strong broadening of the Rayleigh line, whose tail is extended through entire measured spectral range from 20 to 300 cm⁻¹, overlapping fine details of the metal nanoparticle spectra. It is the reason why the Raman spectra of the composite materials were measured at the liquid-nitrogen temperature (Figs. 1a and 1b). Unlike the Raman measurements performed at 300 K, the spectrum of the Ag : SiO₂ sample (Fig. 1a) contains two weak peaks at $\nu_1 = 28$ cm⁻¹ and $\nu_2 = 82$ cm⁻¹, and the spectrum of the Cu : SiO₂ sample has one weak peak at $\nu = 102$ cm⁻¹ (Fig. 1b). Based on the model considered in [3–7], in which the existence of the peak in this range of the Raman spectrum is associated with acoustic vibrations in spherical metal nanoparticles of certain sizes, we can estimate the nanoparticle size. The size is estimated using the relationship between the frequency shift in the Raman spectrum ν (cm⁻¹), particle diameter d , and mean transverse velocity of sound V_t

$$\nu = 0.85 \frac{V_t}{dc}, \quad (1)$$

where c is the velocity of light in free space [4]. According to this approach, we have analyzed the Raman spectra measured in this work (Figs 1a and 1b) using known values $V_{t(\text{Ag})} = 1660$ m/s [4] and $V_{t(\text{Cu})} = 2260$ m/s [16]. In this case, the peaks $\nu_1 = 28$ and $\nu_2 = 82$ cm⁻¹ in the spectrum of the Ag : SiO₂ sample (Fig. 1a) can demonstrate the existence in the sample of two dominant groups of spherical silver nanoparticles with the mean diameters $d_1 \approx 1.6$ nm and $d_2 \approx 0.6$ nm, respectively. This assumption well agrees with the results of [12, 17, 18], where the electron microscopy examination of cross-section cuts of the silicate glass with ion-synthesized metal nanoparticles and the measurement of the reflection spectra showed that, in the case of the low-energy implantation of metal ions, two layers containing ensembles of nanoparticles of different sizes locally separated in depth can be formed. In this case, larger metal nanoparticles are arranged closer to the surface within the ~20-nm-thick layer and smaller nanoparticles are at a more depth within ~50-nm-thick layer. In the case of high-energy implantation of Cu⁺ ions whose energy (160 keV) was substantially higher than the energy of Ag⁺

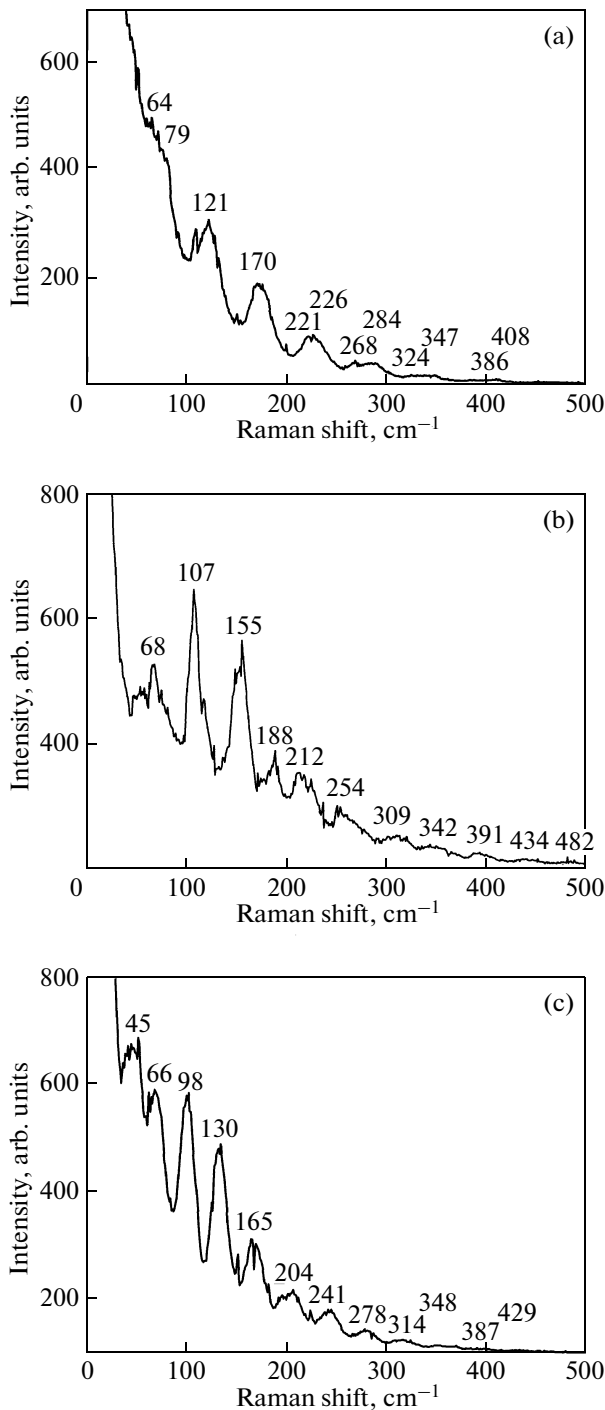


Fig. 2. Raman spectra of the SiO₂ sample with silver nanoparticles at $T = 77$ K after pulsed laser annealing ($\lambda = 694$ nm, $\tau_l = 75$ ns) with the energy densities $W =$ (a) 0.86, (b) 0.95, and (c) 1.4 J/cm².

ions (60 keV), the appearance of the single peak $\nu = 102$ cm⁻¹ in the Raman spectrum shows that the Cu : SiO₂ sample contains only one set of spherical Cu nanoparticles with the mean size $d \approx 0.6$ nm. Unlike the Ag : SiO₂, the distribution profile of metal nano-

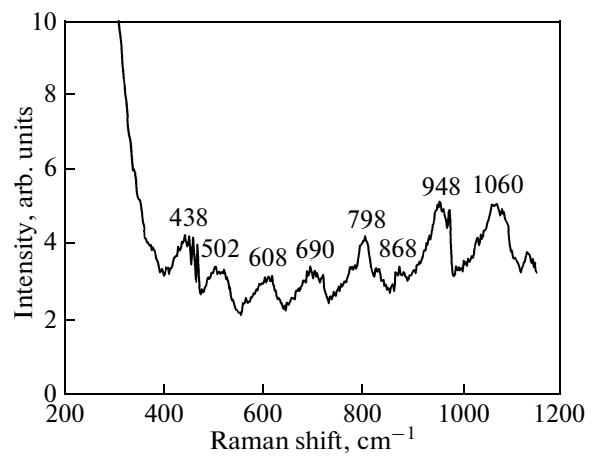


Fig. 3. Raman spectrum of the SiO₂ sample with copper nanoparticles at $T = 77$ K after pulsed laser annealing ($\lambda = 694$ nm, $\tau_l = 75$ ns, $W = 1.0$ J/cm²).

particles in depth is not influenced by the nearby surface, as it is the case upon the low-energy ion implantation [10, 11].

The irradiation of the implanted samples by nano-second single ruby laser pulses with different power densities at a wavelength belonging to the spectral region of the plasmon absorption of the ion-synthesized metal nanoparticles substantially changes the Raman spectra measured at 77 K (Figs. 2a–2c and 3), namely, they now contain ten or more of narrow lines. It was found that the number of new peaks in the Raman spectrum of the Ag : SiO₂ sample and the distances between them are dependent on the energy density in a laser pulse (Figs. 2a–2c). At the same time, in the spectrum of the Cu : SiO₂ sample, a set of lines occurs after laser annealing only as the energy density in the pulse was 1 J/cm² (Fig. 3). The interpretation of the spectra shown in Figs. 2 and 3 based on the model of acoustic vibrations in spherical metal nanoparticles (see relationship (1)) leads to the conclusion that the laser irradiation results in the formation of several groups (of an order of ten or more) of metal nanoparticles rigidly calibrated in size. Such a conclusion is unlikely.

Another explanation is provided by the peculiarities of the chosen conditions and regimes of annealing under which there occurs an effective plasmon absorption of the laser radiation by the nanoparticles in a transparent glass. In this case, the nanoparticle shape can be transformed, as it was the case in the silicate glass for ion-synthesized Ti₂S nanoparticles irradiated by laser at the wavelength of the transparency of the matrix of 1064 nm [19]. Previously, in [14, 15], as the laser-annealed glasses containing ion-synthesized metal nanoparticles were studied using an atomic-force microscope, it was assumed that laser annealing cannot only decrease the size of silver nanoparticles in glass but also change its shape from spherical to

Table 1. Comparison of the calculated values of the transverse vibrational modes v_{Ag} in silver nanowires with the length $l_{\text{Ag}} = 2.5$ nm and the experimental values of the Raman shifts ν measured for the Ag : SiO₂ sample after laser annealing at $\lambda = 694$ nm, $\tau_i = 75$ ns, and $W = 1.4$ J/cm² (Fig. 2c)

Order of vibration m	$v_{\text{Ag}}, \text{cm}^{-1}$ (calculation)	ν, cm^{-1} (experiment, Fig. 2c)
1	18.57	—
3	55.7	45/66
5	92.85	98
7	130	130
9	167.13	163/167
11	204.27	204
13	241.41	241
15	278.5	278
17	315	314
19	352	348
21	389	387
23	427.1	429

Table 2. Comparison of the calculated values of the transverse vibrational modes v_{Cu} in copper nanowires with the length $l_{\text{Cu}} = 2.5$ nm and the experimental values of the Raman shifts ν measured for the Cu : SiO₂ sample after laser annealing at $\lambda = 694$ nm, $\tau_i = 50$ ns, and $W = 1.0$ J/cm² (Fig. 3)

Order of vibration m	$v_{\text{Cu}}, \text{cm}^{-1}$ (calculation)	ν, cm^{-1} (experiment, Fig. 3)
1	46.08	—
3	138.24	—
5	230.4	—
7	322.6	—
9	414.78	438
11	506.9	502
13	599.1	608
15	691.3	690
17	783.5	798
19	875.6	868
21	967.8	948
23	1060	1060

extended. In this case, we can expect that, in our experiment, as a result of laser annealing, metal nanoparticles of extended shape comparable with one-dimensional quantum wires are also formed.

Thus, we interpret the peaks in the inelastic Raman scattering spectrum (Figs. 2, 3) using the model of in-phase bending vibrations of the harmonica type in a metal nanostring (quantum wire) [20]. For this purpose, we used in our calculations the classical formula of string vibrations [20]

$$f = \frac{m}{2l} \sqrt{\frac{E}{\rho}}, \quad (2)$$

where f is the frequency of acoustic vibration (s⁻¹), E is the Young's modulus (din/cm²), ρ is the density (g/cm³), l is the quantum wire length, cm; m is the order of vibration (the site numbers along the quantum wire length). It is known that, in the Raman spectrum, the vibration is active at odd values of $m = 1, 2, 3, \dots$ [20]. The quantity f was calculated using table values of corresponding parameters for silver and copper as follows [16]: $E_{\text{Ag}} = 8.27 \times 10^{11}$ din/cm², $E_{\text{Cu}} = 12.98 \times 10^{11}$ din/cm², $\rho_{\text{Ag}} = 10.5$ g/cm³, and $\rho_{\text{Cu}} = 8.92$ g/cm³. In the framework of this model (see relationship (2)), we assume that the peaks observed in the experimental Raman spectrum ν (cm⁻¹) correspond to the transverse vibrational modes in silver and copper quantum wires with the length l : $v_{\text{Ag, Cu}} (\text{cm}^{-1}) = f(\text{s}^{-1})/c$, where c is the velocity of light. Such an approach allows the estimate of the nanowire length. The calculation and experimental data on ν for silver and copper are listed in Tables 1 and 2, respectively. As

follows from the results presented, the best coincidence between the calculated values of the transverse vibrational modes and experimental values of the Raman shifts is at the wire lengths $l_{\text{Ag}} = 2.5$ nm and $l_{\text{Cu}} = 1.38$ nm. Note that, in the Ag : SiO₂ sample, only one set of silver nanoparticles is observed after laser annealing, not two sets, as after the implantation. It confirms the phenomenon observed earlier during laser annealing of similar samples, namely, the effective melting of smallest and conservation of large metal nanoparticles [21], which likely occurs also in our case after laser annealing.

4. CONCLUSIONS

Thus, in this work, we measured for the first time, at the liquid-nitrogen temperature, the equidistant spectrum of inelastic scattering of light from copper and silver nanoparticles formed in the glass substrate by the ion implantation followed by laser annealing. The vibrational modes are observed with a high resolution, which permits the quantitative analysis based on current theoretical models for metal nanoparticles. The comparison of the calculated and experimental spectra predicts and demonstrates that laser annealing can change the shape of the ion-synthesized metal nanoparticles from spherical to extended shape.

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SPELL: 1. Kreibig, 2. Faizrahmanov or Faizrahmanov?

