

Nobel Ag-Cu Ion-Exchange Bimetallic Nanoclusters Formation by Tailored Gold Ion (Au^{2+}) Implanted Materials RBS and Optical Study

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Abstract

Technologically driven some glass materials are containing metal clusters have attracted quite attention both in cluster research and in possible futuristic applications of such nanoclusters for magnetic or optoelectronic purposes. In this regard, formation of bimetallic alloys and core-shell nanostructures inside a soda-lime glass were prepared by simple ion-exchange methods and further studied by the optical absorption (OA) properties. Further, we made an attempt for the first time the novel route for the synthesis of bimetallic nanoclusters, gold in various doses was directly implanted in a plain soda-lime glass as well as in a copper and silver ion-exchanged soda-lime glass using the tandem accelerator anticipating the core-shell or alloys phase between the metal species. Also, the post implanted gold (Au^+) metal ions were investigated by Rutherford backscattering spectroscopy (RBS) analysis performed on the Cu and Ag ion-exchanged samples to confirm the presence of bimetallic clusters formed by ion-exchange during implantation.

1. Introduction

In generally, the ion exchange can be defined as the reversible exchange of ions between a liquid-phase and a solid-phase (ion-exchange resin) which is not accompanied by any radical change in the solid structure. Besides, the ion-exchange is a water treatment method where one or more undesirable ionic contaminants are removed from water by exchange with another non-objectionable, or less objectionable ionic substance. Respectively, glasses containing metal clusters have attracted quite some attention both in cluster research and in possible applications of such clusters for magnetic or optoelectronic purposes. Hence, it's exhibit nanometer-sized (NMs) clusters of noble metals in glasses strong absorption of visible light which, in addition, may be highly polarization needs depending on size and shape with special alignment of the clusters. Numerous research methods are trailed to obtain control of the mechanisms to form such clusters. Nobel bimetallic core-shell and alloy nanoclusters could be synthesized by different methods, such as the electrochemical method, radiolysis of aqueous solutions, hydrogen arc plasma, and laser vaporization co-deposition. Bimetallic clusters (alloys or core-shells) represent one of the most promising avenues toward new catalytic systems. Formation of embedded bimetallic nanoclusters by ion-exchange technique is the prime step of various combined methodologies used for the formation metal nanocluster composite glasses (MNCGs). A promising approach is the irradiation of glasses containing the wanted metal as a metal-oxide with heavy-ion energy beams around MeV. This technique has been explored in the case of soda-lime glasses with Cu clusters from Cu_2O in the original mixture of the oxides and with Ag clusters from the incorporation by ion-exchange. In both cases metal-clusters were already produced by other means of treatment, such as heat-treatment in reducing atmosphere and/or laser irradiation.

Bimetallic nanoclusters as alloys or as core-shell structures are attractive materials due to their composition-dependent optical and catalytic properties. These bimetallic nanoclusters have been the focus of extensive research efforts due to their unique surface plasmon resonance in the visible region. Although the composition of the bimetallic nanoclusters is the same, they exhibit different optical

properties corresponding to their respective core–shell or alloy phases. Bimetallic clusters (alloys or core–shells) represent one of the most promising avenues toward new catalytic systems [1]. It has been known for many years that metal mixing (alloying) can significantly modify the catalytic activity and selectivity of a metal [2, 3].

The primary benefit of using bimetallic clusters is the variability of their composition, allowing the cluster reactivity to be tailored to each individual application [4]. Furthermore, by determining the reactivity of small bimetallic particles, it is possible to increase our understanding of the development of bulk behavior, especially concerning the electronic and geometric makeup in metallic entities of finite dimensions [5–7]. It is possible that a new class of materials with tailored properties can be produced starting with clusters as building blocks [8–11]. Mixing of two atoms and expanding the mixture [12–13] produce new clusters that, in the case of metals, are the microscopic analogues of the bulk alloys.

In the case of bulk alloys, different stable phases appear for a given pair of metals, characterized by specific atomic structures and usually by fixed concentrations. Transition to another phase can occur when a critical temperature is reached. Also, some of those phases can be stable over an extended range of atomic concentrations, especially for alloys very rich in one of the components. Formation of embedded bimetallic nanoclusters by ion-exchange technique is the prime step of various combined methodologies for the formation metal nanocluster composite glasses (MNCGs).

It involves the introduction of the metal ions of interest into the dielectric glass matrix and is made to aggregate by means of proper subsequent treatments such as low mass ion irradiation, heat-treatments in reducing atmosphere, and pulsed laser irradiation. In this multi-step process, metal aggregation in nanometer sized (nm) clusters is promoted with several degrees of freedom. Also, the formation of bimetallic alloy and core–shell nanostructures inside the soda-lime glass by the above technique along with their optical properties are discussed. Also, for the first time as a novel route for the synthesis of bimetallic nanoclusters, gold in various doses was directly implanted in a plain soda-lime glass as well as in a copper and silver ion-exchanged soda-lime glass, using the tandem accelerator anticipating the core–shell or alloy phase between the metal species. Furthermore, ion-implantation is a material surface modification process by which ions of a material are implanted into added solid material, causing a change in the surface physical and chemical properties of the materials. Ion implantation involves an ion source (where ions of the desired element can be produced), an accelerator (where the ions are electrostatically accelerated to a high energy) and a target (where the ions impinge on a target). The energy of the ions, as well as the ion species and the composition of the target, determine the functions acquired and the depth of penetration of the ions in the solid.

2. Bimetallic Cu-ag And Ag-cu Nanoclusters Formation

Formation of bimetallic Cu-Ag and Ag-Cu nanoclusters is achieved by the sequential ion-exchange technique followed by furnace annealing and laser irradiation for different exposure timings. Pre-cleaned soda-lime glass is first dipped in a molten copper salt bath first and then again dipped in a molten salt

bath of silver for Cu-Ag ion exchange. The process is repeated in the reverse manner by dipping in the silver bath first and then in the copper bath for the Ag-Cu ion-exchange. The Cu-Ag and Ag-Cu ion-exchanged samples were then cleaned and then irradiated with laser for different exposure timings. Optical absorption spectra of the laser irradiated samples were recorded in the wavelength range of 200–1200 nm at room temperature and the spectra are shown in Figs. 1 and 2. It can be observed from Fig. 1 that there are two surface plasmon resonance (SPR) peaks, one centered at 420 nm due to silver and another shoulder centered at 564 nm due to the copper clusters [19–20]. The absorption spectra (OA) resembled the Cu-coated Ag nanocrystals in silica formed by sequential implantation of Ag^+ and Cu^+ ions with, TEM analysis depicting the diffracting rings of the core and shell materials as reported by Anderson et al. [14].

It is also clear from the graphs that for various laser exposure timings the spectra have slight shifts in their peak positions, which may be due to the variation in the concentration of the respective metal species, since the SPR peak position depends on the concentration of the respective metal species. Hence it can be very well confirmed that the laser irradiation of the Cu-Ag ion-exchanged samples resulted in the formation of Cu-coated Ag nanoclusters embedded in a soda-lime glass and are not simply Cu and Ag nanoclusters scattered inside the dielectric medium. To confirm the same, the optical absorption of pure Cu, Ag, and Au nanoclusters in soda-lime is shown in Fig. 3 for reference. In the case of Ag-Cu ion-exchanged and laser-irradiated samples, the spectra exhibited in Fig. 2 shows only one broad peak centered at 425 nm with a slight hump centered at 505 nm. Spectra of this kind are only due to the Ag-coated Cu nanoclusters inside the soda-lime glass as confirmed earlier [14]. No significant variation in peak positions is observed for the different exposure timings. The reason for the presence of significant broad silver peaks alone is because of laser irradiation of AgCu ion-exchanged samples, resulted in an interesting phenomenon of evolution of silver peak with the dissolution of the already formed copper clusters, as the scattered silver atoms start clustering at the cost of the already formed copper clusters resulting in the dissolution of them.

3. Implantation Of Au^{2+} In Cu And Ag Ion-exchanged Soda-lime Glass

The Au^{2+} ions were implanted in both the Cu and Ag samples for three different doses (1×10^{17} , 5×10^{16} and 7×10^{16} ions/cm²) and were subjected to optical absorption studies. After implantation of gold, Rutherford backscattering analysis was performed on the Cu- and Ag ion-exchanged samples to confirm the presence of bimetallic clusters formed by ion-exchange during implantation.

Rutherford backscattering spectrometry (RBS) is an analytical technique used in materials science. RBS is used to determine the structure and composition of materials by measuring the backscattering of a beam of high energy ions impinging on a metal. A method of determining the concentrations of various elements as a function of depth under the surface of a sample, by measuring the energy spectrum of ions which are backscattered emitted energy beam directed at the surface. Rutherford backscattering as an elastic collision between a high kinetic energy particle from the incident beam (the projectile) and a stationary particle located in the sample. Elastic in this context means that no energy is either lost or

gained during the collision. Optical absorption spectra of the Cu and Ag samples implanted with Au²⁺ ions are shown in Figs. 4 and 5, respectively.

The absorption peak in Fig. 4 is found to be centered at 560 nm for the first Au²⁺ implantation dose of 5×10^{16} ions.cm⁻². This SPR peak is due to the alloying phase between the two metal Cu and Au species, because the peak position is in between the SPR position of pure copper (565 nm) and pure gold (525 nm) nanoclusters in the soda-lime glass [15]. With further increase in the implantation dose, the SPR peak is found to have a blue shift, which is very clear from the spectra. Any shift in the peak position can be attributed to the increase in the concentration of any one of the metal species. Thus, the blue shift of the SPR peak with an increase in Au²⁺ concentration is in agreement with the trend reported earlier [15], with the SPR peak shifting toward that of the pure Au nanocluster, with peak centered at 554 nm for the highest implantation dose of 1×10^{17} ions.cm⁻². From Fig. 5 it can be observed that the spectra exhibited only one peak centered at 426 nm for an Au²⁺ implantation dose of 5×10^{16} ions.cm⁻². This peak is attributed to the intermediate alloying phase between the Ag and Au metal species for the initial implantation doses reported by earlier researchers [16]. But for the 7×10^{16} ions.cm⁻² implantation dose, the SPR peak shows a red shift with peak centered at 484 nm.

This is purely due to alloying between the two metals with the SPR shifting from silver side to that of gold with an increase in its concentration. But this alloy phase disappears for the higher implantation dose of 1×10^{17} ions/cm² and the SPR shifts to the 428 nm again. Thus, a transient alloy phase was perceived with a red shift of absorption spectrum for the intermediate implantation dose. Such kind of intermediate alloy phase and transient alloying between the Ag and Au metal species has been reported.

In the present study, the depth profiling of implanted gold in soda glass is carried out using RBS technique with 2 MeV He⁺ ions. The recorded RBS spectra for Au²⁺ implanted in Cu and Ag ion-exchanged samples are shown in Fig. 6 and Fig. 7, respectively. Figures 6 & 7 reveal the presence of glass components like O, Na, and Si present in pure soda-lime glass. The peaks were identified and were matching with the values predicted earlier studies [17, 18]. Also, it is clear from the spectra that both Cu-Au and Ag-Au were present in the respective Cu and Ag ion-exchange and Au²⁺ implanted glass. An increase in the concentration of the Au is well observed with an increase in implantation dose with the intensity of the peaks increasing.

4. Conclusion

Dissolved copper clusters are impregnated by the clustering silver atoms to form Ag-coated Cu nanoclusters inside the dielectric matrix. Thus, the embedded bimetallic Cu-coated Ag and Ag-coated Cu nanoclusters were formed in a soda-lime glass by a commercial sequential ion-exchange technique followed by laser irradiation with different exposure timings. The presence of the core-shell structures is also confirmed by their respective optical absorption spectra. The optical absorption studies unveiled the formation of intermediate and transient alloy phases between the metallic species with the implantation

of gold in Cu and Ag ion exchanged glasses with the RBS analysis supporting the results. To conclude, by combining the results of optical absorption analysis with that of the RBS it can be stated that embedded bimetallic nanoclusters of different states like core-shell structures or alloy nanoclusters along with intermediate alloy phases were formed in soda-lime glass could be acted as noble metal substrates for NLO, and bio-medical pathogenic materials identification and future drugs career in the noninvasive process.

Declarations

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Conflicts of interest/Competing interests

All the authors declare no conflict of interests. The authors declare that they have no known competing financial interests or personal relationships which have, or could be perceived to have, influenced the work reported in this article.

Availability of data and material

Research Samples and scientific data of the compounds are available from the authors

Ethical approval

This article does not contain any studies with human participants or animals performed by any of the authors.

Code availability

Based on the request will be provide from the corresponding author.

Author contributions statement

A.R.F., P. M., D. M. P.S.R., and E.M. – Designed Experiments; Manuscript Preparation, E.M., D. M., M. M. and D.M. - Conducted Experiments, Acquired Data, Supervision; P.M., E. M., and D.M. – Drafted Manuscript, Editing, Reviewing; E.M., D.M., S.U., M.M., and E.M. – Novel Ideas, Editing, Formal Analysis, Methodology, Data Interpretations, Scheme Administration, Combined Discussed, Results, Commented Manuscript. D. M. and M. M.— Review, Re-editing, Comprising Work, Internal Funding acquisition; E. M. – Resources, Visualization & Conceptualization, Finalizing Work.

Additional information

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References

1. Somorjai GA, Surface Chemistry and Catalysis Wiley, New York, (1994)
2. Sinfelt JH, Bimetallic Catalysts: Discoveries, Concepts, and Applications Wiley, New York, (1983)
3. Ponc V (1983) Adv Catal 32:149
4. Gonzolez RD (1984) Appl Surf Sci 19:181
5. Lopez GE, Freeman DL (1993) J Chem Phys 98(2):1428
6. Nakajima A, Kishi T, Sugioka T, Kaya K, Chem. Phys. Letters 187, (3) (1991)
7. Lopez MJ, Marcos PA, Alonso JA (1996) J Chem Phys 104(3):1056
8. Khanna SN, Jena P (1992) Phys Rev Lett 69:1664
9. Castleman AW Jr, And RG, Keesee (1988) Science 241:36
10. Castleman AW Jr (1990) J Cluster Sci 1:3
11. Castleman AW Jr, Bowen KH (1996) J Phys Chem 100:12910
12. Kappes MM, SchP M, Schumacher EJ (1987) J Phys Chem 91:658
13. Lbpez MJ, lliiguez MP, Alonso JA (1990) Phys Rev B 41:5636
14. Anderson TS, Magruder RH III, Wittig JE, Kinser DL, Zuhr RA (2000) Nucl Instr Meth B 171:401
15. Battaglin G, Cattaruzza E, de Julian C, Fernandez et al (2001) Nucl Inst Methods In Physics B 175–177:410–416
16. Izgaliev AT, Simakin AV, Shafeev GA, Bozon-Verduraz F (2004) Chem Phys Lett 39:467–471
17. de Marchi G, Caccavale F, Gonella F, Mattei G, Mazzoldi P, Battaglin G, Quaranta A (1996) Appl Phys A 63:403
18. Gangopadhyay P, Magudapathy P, Kesavamoorthy R, Panigrahi BK, Nair KGM, Satyam PV (2004) Chem Phys Lett 388:416–421
19. Manikandan P et al (2014) Structural, Optical and Micro-Raman Scattering Studies of Nanosized Copper Ion (Cu⁺) Exchanged Soda Lime Glasses. Plasmonics 9(3):637–643

20. Manikandan E, Satpathy G, Chandra GK, Mahapatra DR, Umapathy S (2020) Pathogenic Escherichia coli (*E. Coli*) detection through tuned nanoparticles enhancement study. *Biotech Letters* 42(5):853–863
21. Manikandan P et al (2014) Surface enhanced Raman scattering (SERS) of silver ions embedded nanocomposite glass. *Spectrochimica Acta Part A: Mol Biomol Spect* 124:203–207

Figures

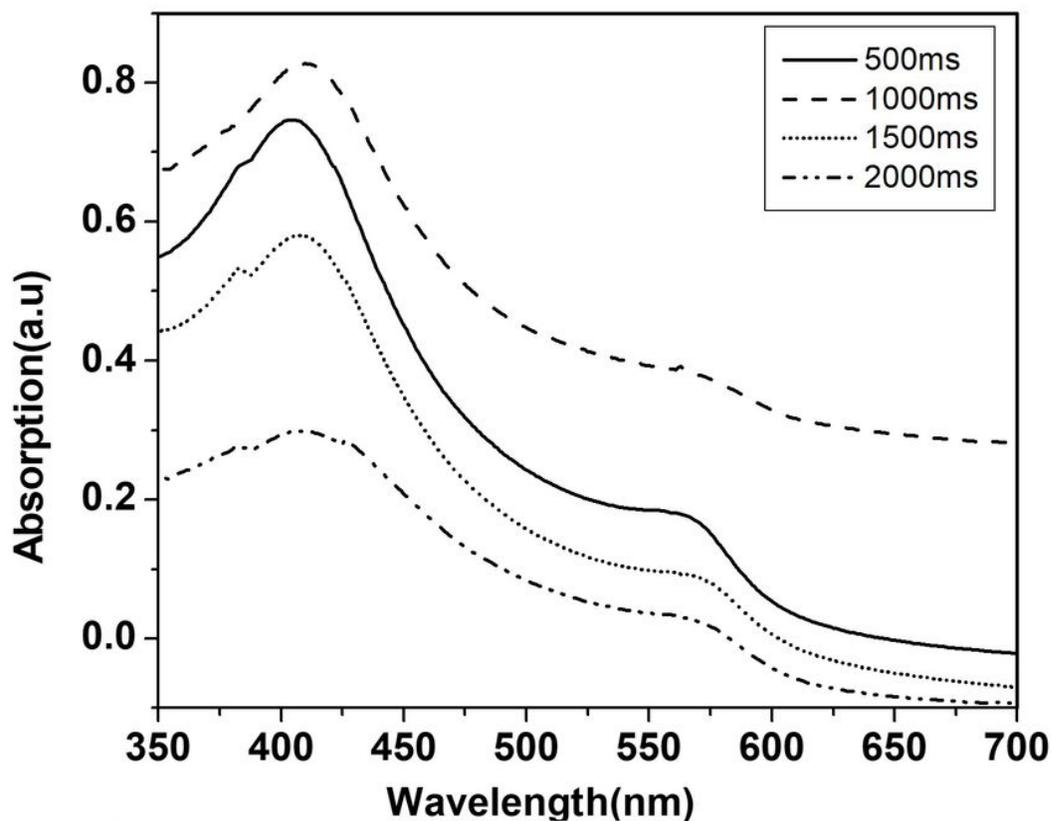


Figure 1

Optical Absorption Spectra for Cu-Ag ion-exchanged and laser-annealed Soda lime Glasses

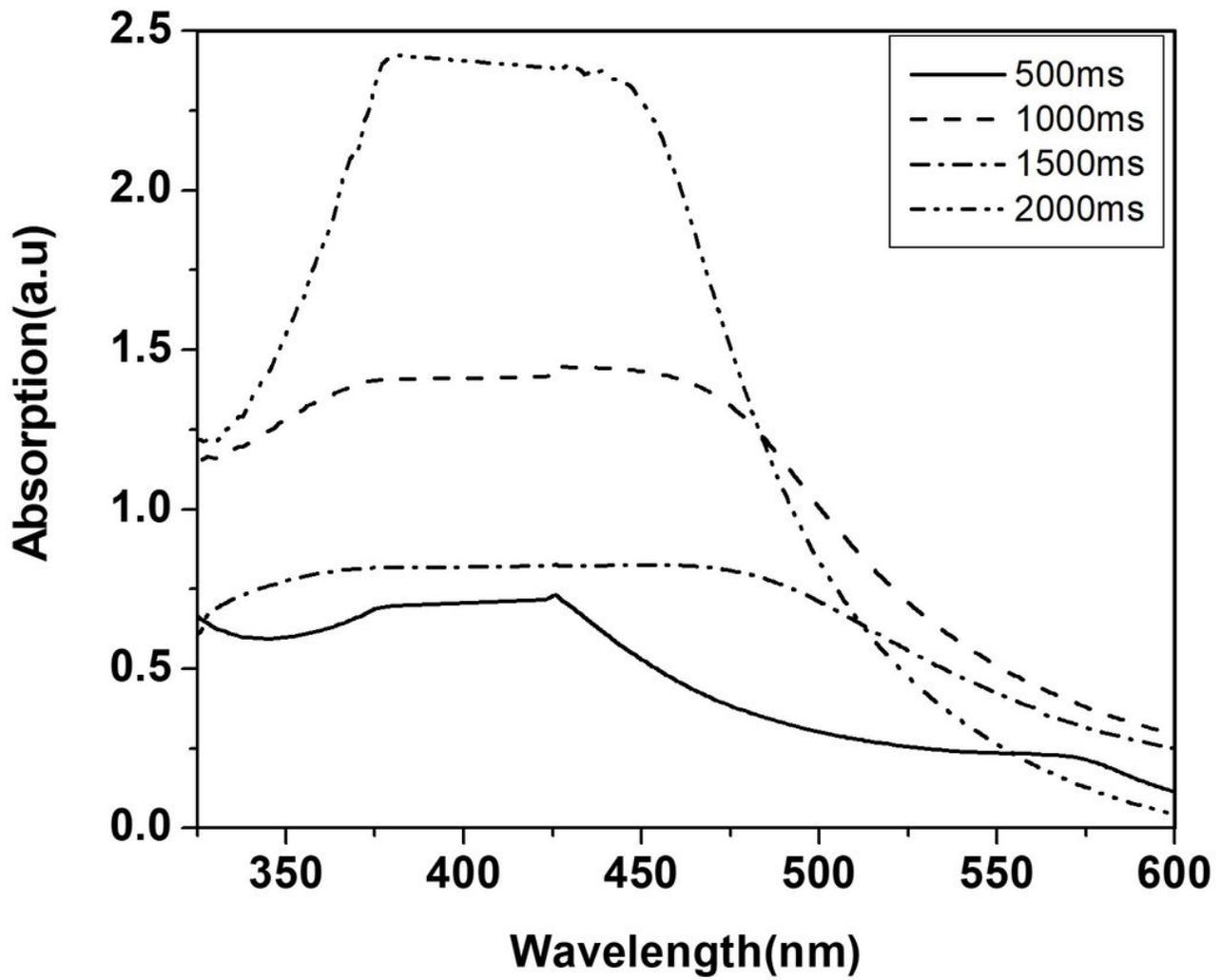


Figure 2

Optical absorption spectra for Ag-Cu ion-exchanged and laser-annealed Soda lime Glasses

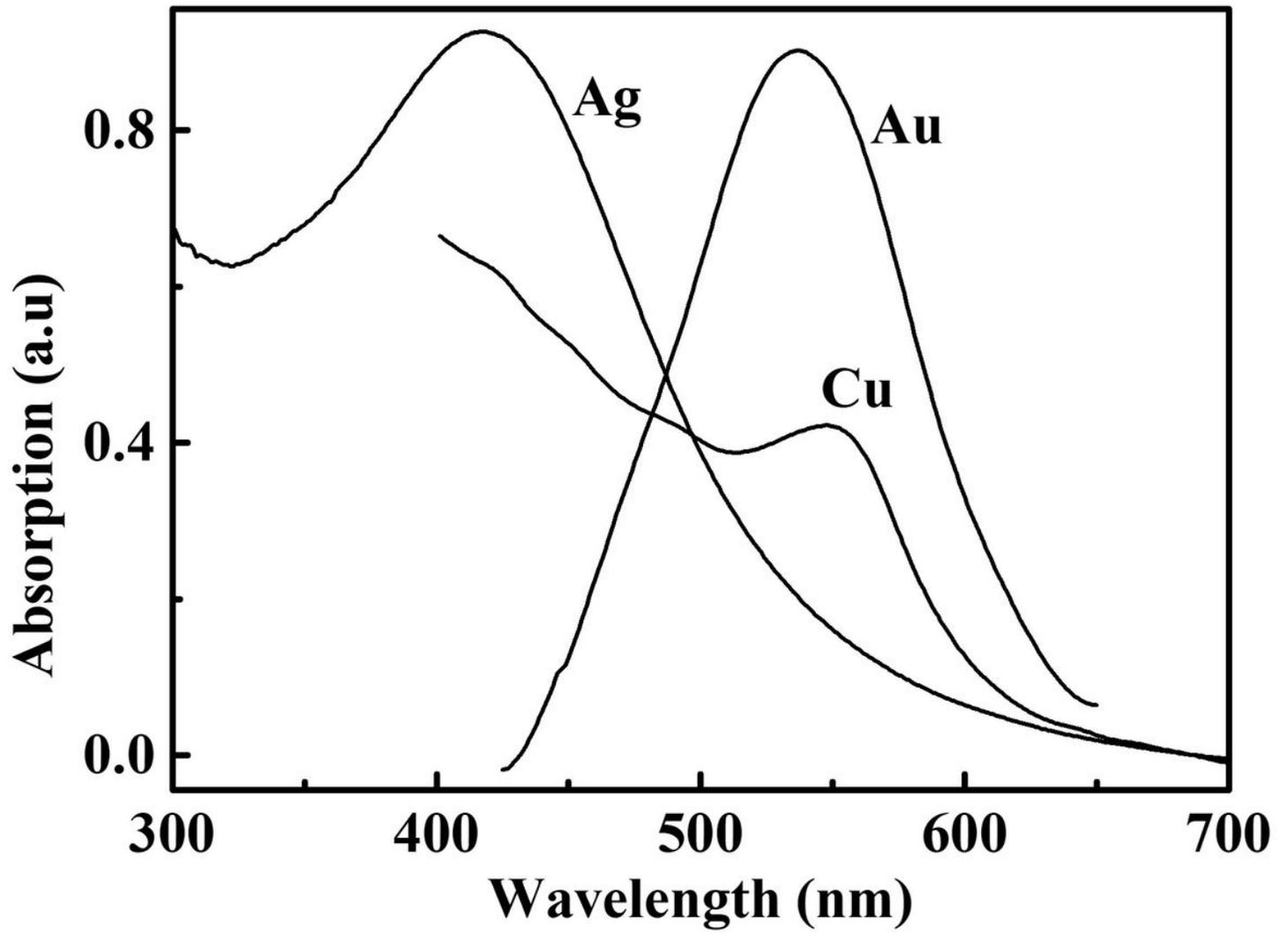


Figure 3

Optical absorption spectra of pure copper, silver, and gold nanoclusters in soda-lime glass

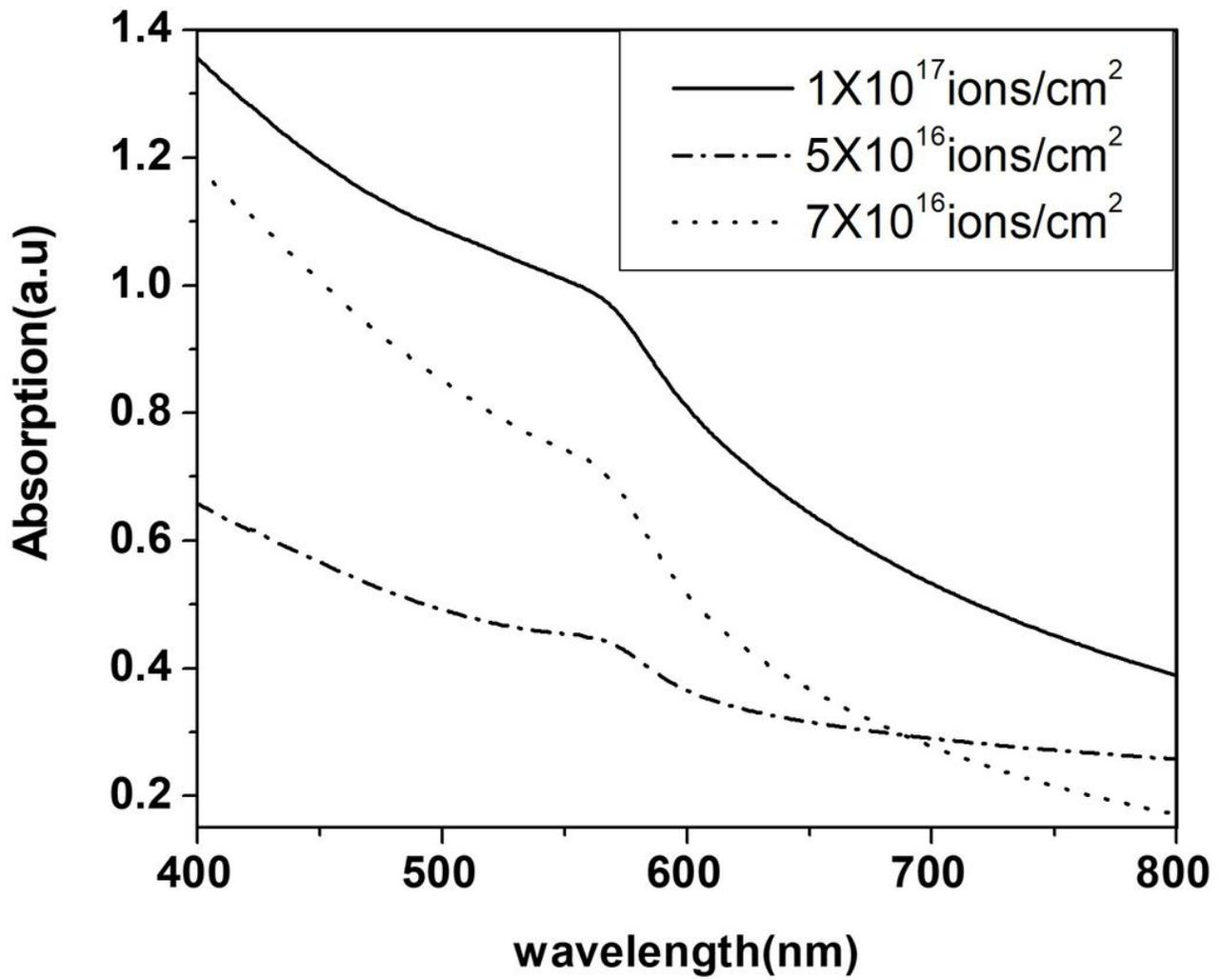


Figure 4

Optical absorption spectra of copper ion-exchanged glass implanted with Au²⁺ ions for various doses.

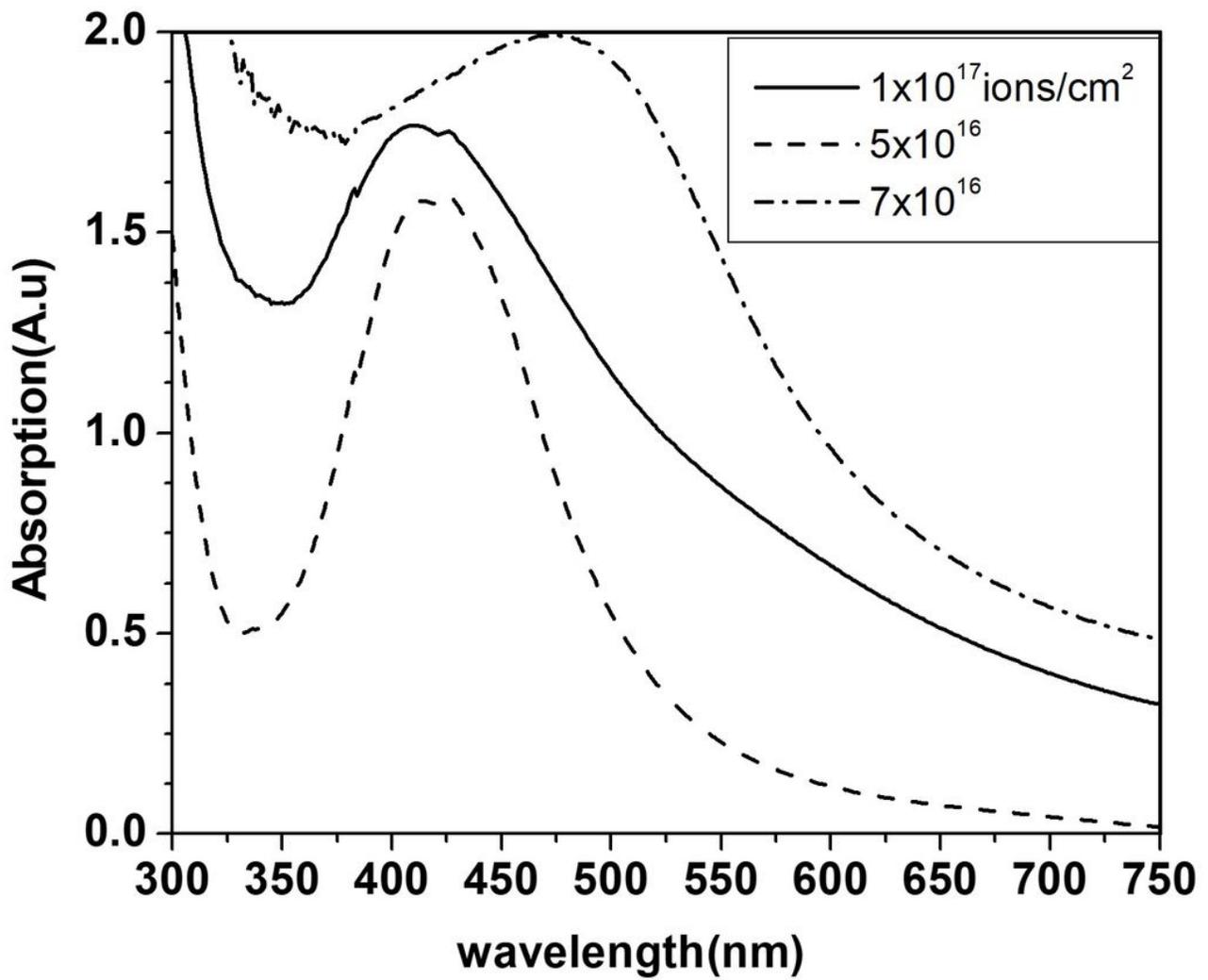


Figure 5

Optical absorption spectra of silver ion-exchanged glass implanted with Au²⁺ ions for various doses.

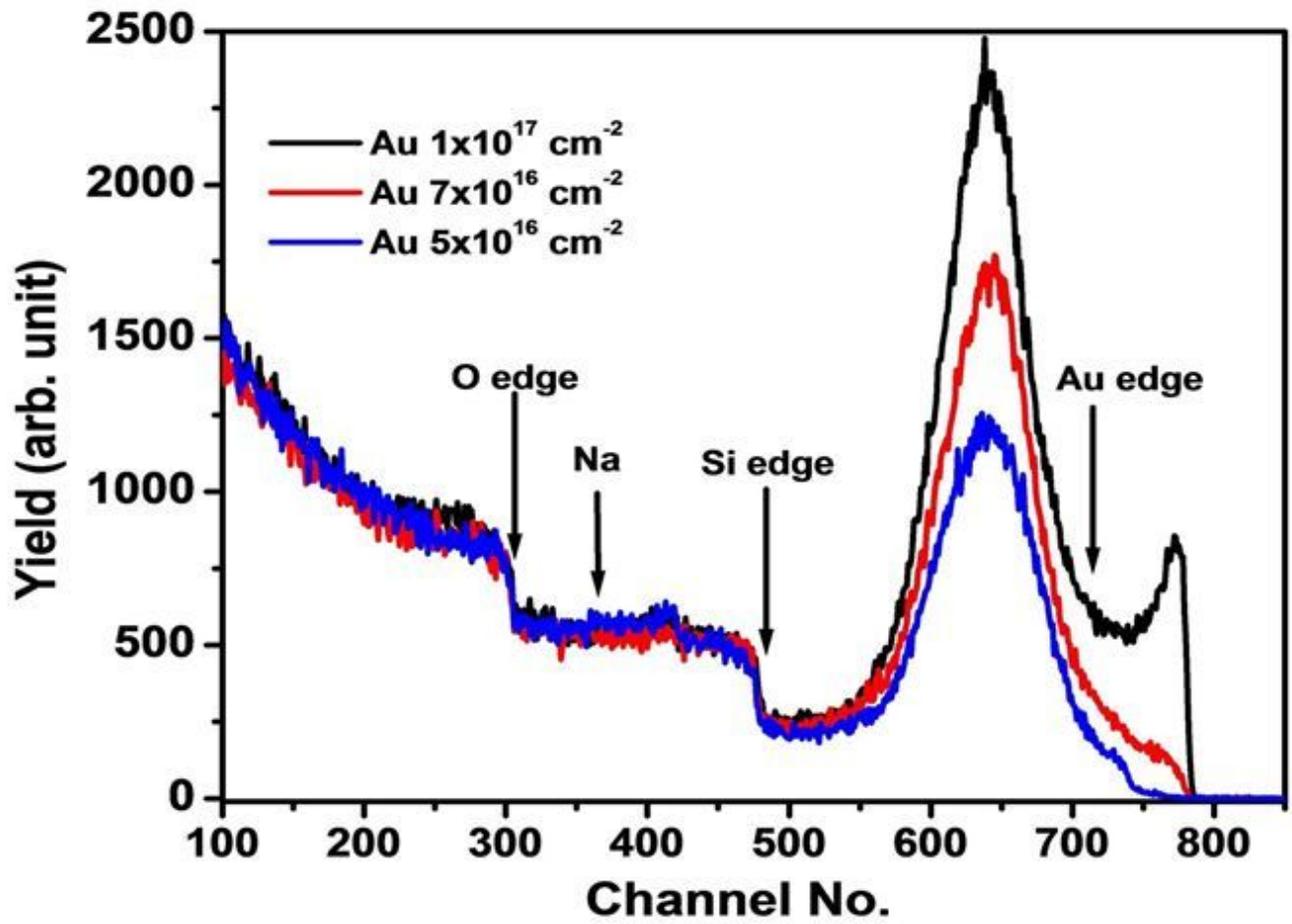


Figure 6

RBS Spectrum of Cu ion-exchanged soda-glass implanted with Au²⁺ ions

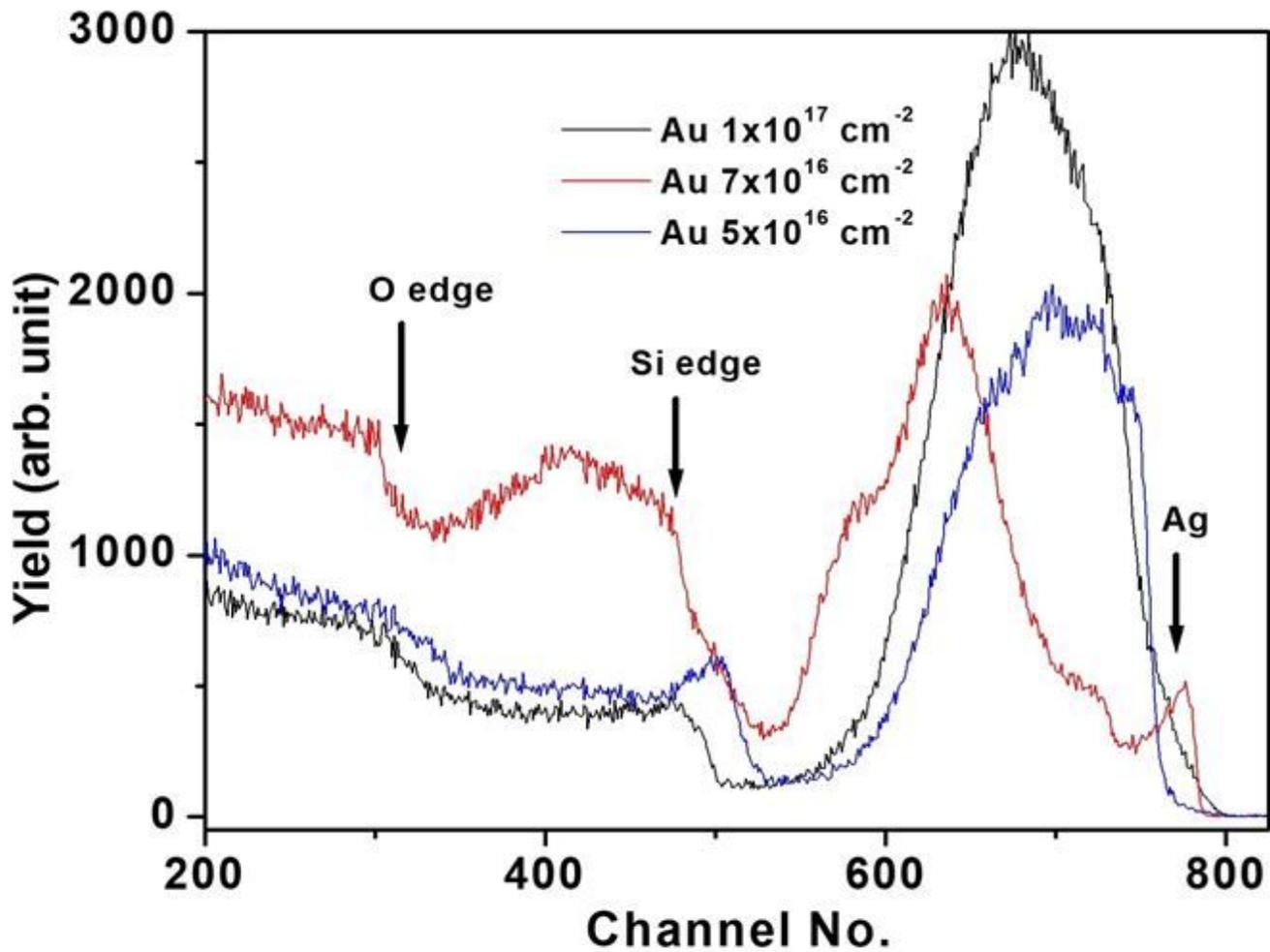


Figure 7

RBS Spectrum of Ag ion-exchanged soda-glass implanted with Au²⁺ ions

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