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METAL NANOCLUSTER COMPOSITE SILICATE GLASSES

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Abstract. Composite materials made by metal clusters embedded in silicate glass matrices exhibit striking optical properties, interesting for photonic application, as well as important magnetic properties, such as superparamagnetism. These composites are also good candidates for application in catalysis and sensor technology. Furthermore, metal clusters can act as sensitizers in rare earths-containing glasses, important in telecommunication technology. Among the most interesting preparation methods of metal nanocluster composite glasses are those based on ion implantation or ion exchange techniques, in combined methodologies that involve also subsequent annealing and/or irradiation of the metal-doped glass matrices. In this work, a short presentation is made of recent developments in the glass composites synthesis that use the combination of different methods, with special emphasis given to those based on ion implantation and ion exchange techniques. Some example will be also presented, that show the effectiveness of combining different techniques for controlling the nanocluster structure and size and thus the material features.

1. INTRODUCTION

Composite materials made by metal clusters embedded in glass matrices have been used for artistic purposes by Roman glass-makers since the fourth century A.D. Architects then exploited their optical properties for the design of the medieval cathedral windows through several European countries. In fact, beautiful glass colors are due to the nanosized metal particles embedded in the matrix [1]. At present, metal nanocluster composite glasses are the object of numerous studies for application in several fields, and the attention dedicated to this topic is witnessed by the increasing number of related contributions at MRS (Materials Research Society), REI (Radiation Effects in Insulators), IBMM (Ion Beam Modification of Materials) and NCM (Non-Crystalline Materials) Conferences. These composite glasses exhibit striking optical properties, for example third-order nonlinearity, interesting for photonic application in all-optical devices [2]. Moreover, a significant enhancement of the fluorescence properties of rare earths-containing glasses is realized by the introduction of metal nanoclusters in the glass matrix [3]. Nanoclusters dispersed in silicate glasses matrices exhibit also important magnetic properties, such as superparamagnetism, enhanced coercivity and shift of the hysteresis loop [4-6].

Glass-based composites are in general expected to play an important role as materials for various nanotechnology applications, due to the potentially low cost, the ease of processing, the high durability, the resistance and the high transparency, with the possibility of tailoring the behavior of the glass-based structures. A significant part of the applied research on glass is therefore currently focused on the definition of suitable methodologies for controlling the behavior of these glass-based materials. Besides the interest for their tech-

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nological application, these glasses are also studied from more basic viewpoints, such as the dynamics of clusters nucleation and growth, their stability, and their structure in terms of composition, crystalline phase, size, and size distribution.

A great effort has been made to develop novel preparation methods, among which are those based on ion implantation techniques [7] and irradiation techniques of metal-doped glass matrices [8,9]. Furthermore, by means of the ion exchange technique, it is possible to dope silicate glasses with metal species to concentration values well beyond (orders of magnitude) the solubility limit [10,11], and subsequent laser [12-14] or ion irradiations [15] may then promote in a controlled way the aggregation and the formation of dimeric or multimeric structures, as well as of nanoclusters. In this work, a short discussion is presented on some recent developments in these novel combined methodologies, with special emphasis to those based on ion implantation and ion exchange routes.

2. ION IMPLANTATION BASED SYNTHESIS

Among the methods of preparation of composite nanostructured glasses, new methodologies have been proposed in which ion implantation is the first step of sequential treatments involving thermal annealing in controlled atmosphere, or laser and ion irradiation [7]. Ion implantation has been explored since the last decade as a useful technique to produce nanocomposite glasses. A large number of experimental work as been done so far by several groups studying ion implantation in glass, in which implantation and proper subsequent treatments effectively promote the formation of nanoclusters [2,15-17]. Along with the experimental activity focused in the material properties for technological applications, several studies are being carried on for describing the physics and chemistry of cluster nucleation and growth [18,19]. An exhaustive phenomenology is still lacking, considering the complex roles played by the chemistry of the elements, the thermodynamics of compound formation, and the thermal or radiation-enhanced diffusion phenomena.

Fig. 1 summarizes the results of several different experimental observations [16], showing the chemical bonds of the element implanted in silica glass as a function of its concentration. It is clear that the local concentration plays a significant role. It is worth underlining that the implanted element

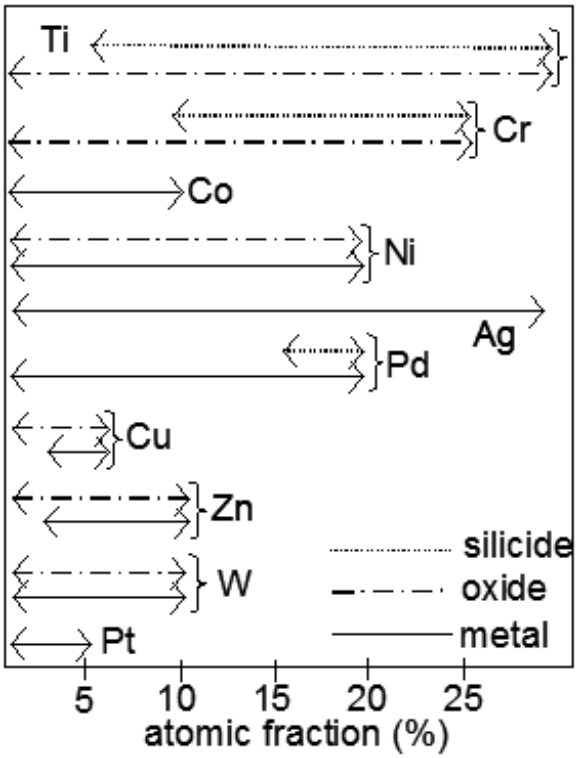

Fig. 1. Chemical bonds of the element implanted in silica glass as a function of its concentration.

distribution is not homogeneous in the implanted region, and thus one has to expect the presence of different nanoclusters in terms of both size and structure in the same implanted sample. Subsequent thermal treatments can effectively modify this scenario, but without an actual control of the cluster growth and structure.

More recently, sequential ion implantation of two different elements has been used to obtain nanoaggregates of binary compounds [20-24]. In particular, the non-equilibrium character of the implantation process may give rise to compounds that would not be stable in the corresponding bulk phase. A Danfysik high-current 1090 implanter was used in the implantation experiments, with ion beam energy values up to 200 keV and current density of the order of 1 $\mu A/cm^2$. Annealings were realized in three different atmospheres, namely, air, H_2-Ar mixture (5% H_2), and pure Ar, in order to study the chemical role of the atmosphere in the clusterization process. Annealing times ranged from 15 min to 5 hrs, while temperatures varied in the range 400-900 °C for silica glass. In general, annealing parameters were chosen to separately study their respective role in giving rise the observed cluster

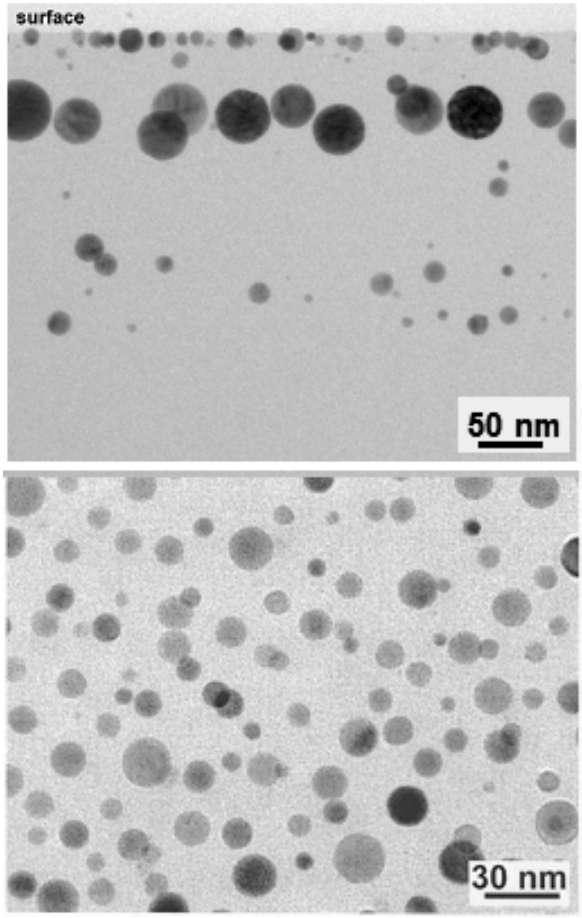

Fig. 2. Transmission electron microscopy pictures of double-implanted silica glass samples: (a) cross-sectional micrograph of Au+Cu implanted system, annealed in H_2 atmosphere; (b) planar micrograph of Au+Ag implanted system, annealed in air.

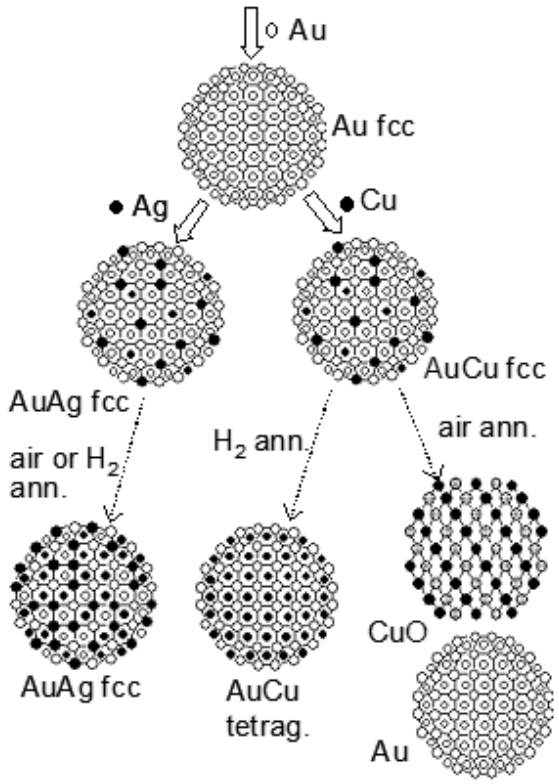

Fig. 3. Pictorial representation (not to scale) of the behavior of Au+Ag and Au+Cu after sequential implantation and subsequent different thermal annealing treatment.

structures. For example, the combined choice of annealing atmosphere and temperature, together with a proper sequence of treatments, were observed to be quite critical in the formation of different composites in double-implanted systems. In the case of annealing treatments performed on soda-lime glasses, the process temperature was 500 °C, so preventing glass softening.

Fig. 2 shows two transmission electron microscopy examples of double sequential implantation in silica, made with the respective couples Au+Cu (Fig. 2a, cross-sectional view) and Au+Ag (Fig. 2b, planar view). In the examples of Fig. 2, the implantation fluences for the Au+Cu sample were $3 \cdot 10^{16}$ atoms/cm^2 at 190 keV of energy for gold ions, and $3 \cdot 10^{16}$ atoms/cm^2 at 90 keV of energy for copper ions. After implantation processes, the sample was also heat-treated at 900 °C for 1 hour in a reducing H_2-rich atmosphere. In the case of the Au+Ag sample, the implantation fluences were $3 \cdot 10^{16}$ atoms/cm^2 at 190 keV of energy for gold ions, and $6 \cdot 10^{16}$ atoms/cm^2 at 130 keV of energy for silver ions. After implantation processes, the sample was also heat-treated at 800 °C for 1 hour in air. For both systems, optical absorption spectroscopy and energy dispersion measurements performed along with TEM microscopy confirmed the formation of alloy (AuCu and AuAg) nanoclusters [25]. Moreover, combination of subsequent heat-treatments in different atmospheres [7] allowed to tailor the composition and structure of the nanoaggregates, promoting de-alloying phenomena that suggest a further degree of freedom in the control of the nanostructure system. As concerns the Au+Cu and Au+Ag implantations, Fig. 3 illustrates the experimental results: after the gold implantation, fcc Au clusters are observed to form. A subsequent implantation of either Ag or Cu gives rise to the formation of alloy AuAg and AuCu clusters, in the form of fcc solid solution richer in gold. In the case of the AuAg system, an annealing treatment in either

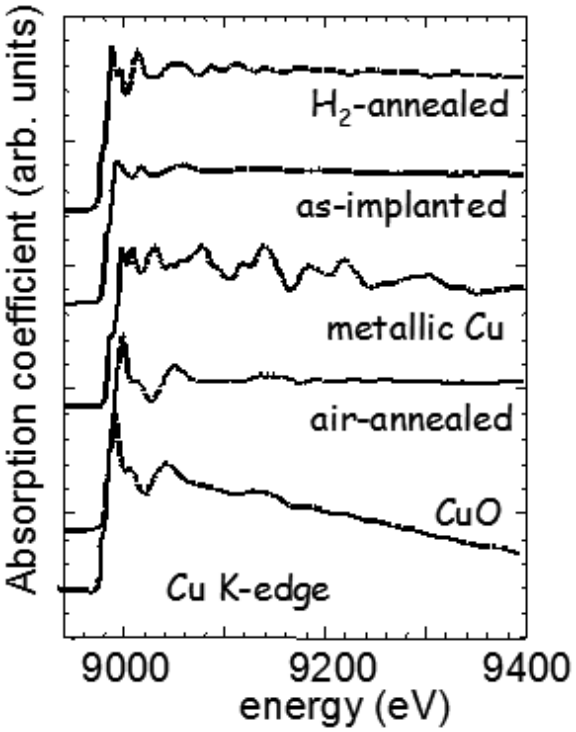

Fig. 4. EXAFS absorption spectra collected at Cu K-edge for Cu+Au implanted SiO_2 samples, treated at different annealing atmospheres. CuO and metallic Cu standards are also shown.

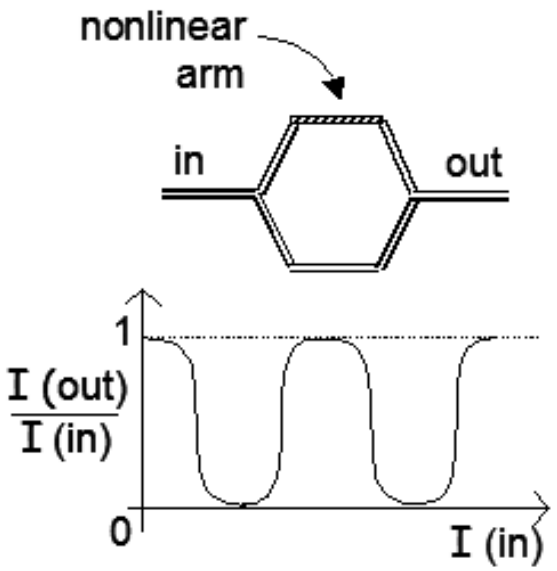

Fig. 5. Mach-Zehnder type device, in which one of the two arms is made of a third-order nonlinear material, and dependence of the output on the input light pulse intensity.

reducing or oxidizing atmosphere gives rise to the enrichment of silver in the cluster, whose size tends to increase. On the other hand, the annealing atmosphere determines different systems in the case of AuCu clusters. The reducing one gives rise to tetragonal AuCu alloy clusters, while the oxidizing atmosphere triggers segregation phenomena leading to the formation of pure gold fcc clusters together with relatively big CuO clusters. In these experiments, the availability of complementary sensitive techniques was particularly important, since often the cluster-rich layers were rather thin (100 nm), and the contemporary presence of different phases made the data analysis difficult. High-resolution transmission electron microscopy, electron diffraction and optical absorption were used in combination with synchrotron radiation based techniques (X-ray diffraction and absorption) used in either transmission or grazing incidence configuration, allowing to follow the formation of the clusters structure during the various steps of the preparation methodology. For example, Fig. 4 shows EXAFS (extended X-ray absorption fine structure) spectra collected at Cu K-edge, for samples made of fused silica sequentially implanted with $3 \cdot 10^{16}$ atoms/cm^2 of copper and gold, at energies such to overlap the implants inside the glass. Metallic copper and CuO spectra are also shown as reference. Spectra are clearly different, allowing a quantitative analysis of the cluster structure, starting from Cu and Au EXAFS spectra. The analysis on the as-implanted sample indicates that clusters of average size 3.8±1.6 nm are formed, with fcc structure, made of $Au_{0.25}Cu_{0.75}$ alloy. Annealing in H-rich atmosphere (at T=900 °C) gives rise to the formation of bigger clusters (average size 8.7±2.5 nm), made of $Au_{0.5}Cu_{0.5}$ alloy, but with con tetragonal structure, while air-annealing promotes the formation of pure gold clusters (average size 33±20 nm), and rather big CuO clusters.

Nonlinear optical properties of gold, silver and copper implanted glasses have been studied by means of the Z-scan technique [26], which can determine the coefficients n_2 and β of the material, related to the nonlinear refractive index and to the nonlinear absorption of a sample; these are defined by $n=n_0+n_2I$ and $\alpha=\alpha_0+\beta I$, where n_0 and α_0 the linear refractive index and absorption, respectively, and I the intensity of the light. These nonlinear properties may play a central role in all-optical switching device technology: Fig. 5 shows for ex-

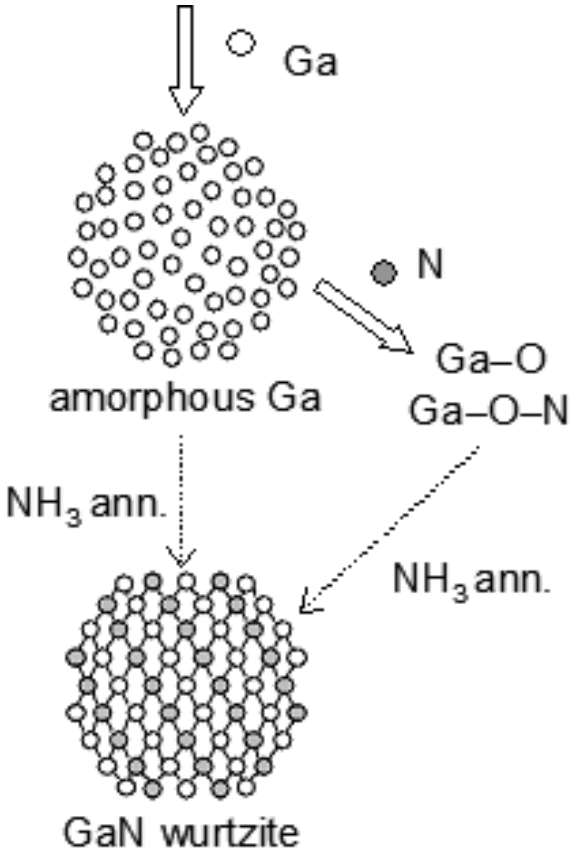

Fig. 6. Pictorial representation (not to scale) of GaN formation upon (double) ion implantation and thermal annealing.

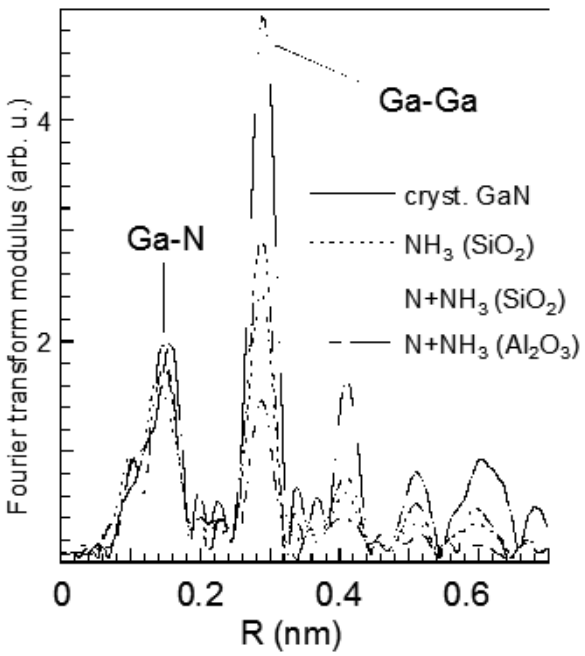

Fig. 7. Fourier transform moduli of *k*-weighted EXAFS spectra for different Ga-implanted samples (silica or Al_2O_3) heat-treated in NH_3 atmosphere, compared with crystalline thin film of GaN.

ample the configuration of a Mach-Zehnder type device, in which one of the two arms is made of a third-order nonlinear material. The phase shift at the output port of the interferometer will depend on the relative speed of the light pulses along the arms, which in turn depends on the intensity of the light pulse travelling the nonlinear arm, because of the nonlinear coefficient of that material. The output could then be selected by selecting the intensity of the pulse at the input, so realizing an all-optical switch. In the case of double-implanted Au+Ag and Au+Cu systems, values of n_2 of the order of 10^{-11} cm^2/W were obtained [27], which are in principles useful for application. On the other hand, the actual feasibility of a third-order nonlinear glass is related to some figures of merit, representing the compromise between the property responsible for its functioning (in this case, the n_2 coefficient), and the parameters that limit the application in actual devices, for example, the linear and nonlinear absorption, and most of all the ratio between the intensity-dependent refractive index coming from electronic processes and the part which is related to slow thermal processes. In the case of the examined systems, a figure of merit is particularly important, namely, $\Phi=F/\tau_{th}$, where F is the ratio between fast and slow n_2 coefficients and τ_{th} is the thermal (slow) recovery time of the material. The figure of merit is an indication of the maximum processing frequency, that for ultrafast application should arrive to exceed the value of 100 GHz. Presently, the examined materials exhibit much lower values for Φ, but promising methods for increasing significantly the figure of merit are being tested, using higher index glasses as substrate and higher values of the volume fraction of the clusters in the matrix. An exhaustive presentation of this topic may be found in references [28,29].

Another interesting implantation experiment, showing the variety of different responses of the involved elements, is that one realized with gallium and nitrogen, sequentially implanted in silica matrices. As depicted in the scheme of Fig. 6, the implant of gallium gives rise to amorphous clusters. Subsequent implantation of nitrogen gives rise to the formation of peculiar compounds, as evidenced by EXAFS spectroscopy [17]. The forma-

tion of wurtzite GaN clusters is reached only after an annealing treatment in NH_3-rich atmosphere, rather independently of the availability of nitrogen in the glass. Fig. 7 shows the moduli of the Fourier transform of the *k*-weighted EXAFS spectra detected at 77K in fluorescence mode at the beamline GILDA of the European Synchrotron Radiation Facility in Grenoble (France). Spectra were collected for Ga-implanted silica glass annealed in NH_3 (with or without previous nitrogen implantation), compared to a sample for which the substrate was Al_2O_3, and crystalline GaN as reference standard. The single scattering theory from wurtzite GaN structure was fitted to the first two shells (Ga–N, Ga–Ga) of the radial pseudo-distribution of atomic distances. EXAFS analysis of the samples evidenced the formation of GaN nanostructures; in particular, quantitative analysis of the structural order in a sphere of radius 0.35 nm around Ga atoms showed the local coordination typical of crystalline GaN, even if an incomplete clusterization of Ga was however observed.

3. ION EXCHANGE BASED SYNTHESIS

Novel preparation methods for metal nanocluster composite glasses use the ion exchange process for introducing high metal dopant doses into the glass. The process is then followed by proper subsequent treatments such as irradiation with low-mass ion beams, heat treatments in reducing atmosphere and pulsed laser irradiation [8,12,14,30,31]. In this way, metal aggregation in nanometer-sized clusters can be promoted with several degrees of freedom for effectively defining the cluster structure and so the performances of the composite material.

Ion exchange in glass, that finds application in the light waveguide technology and in the field of luminescent glasses, is usually performed by immersing silicate glass slides in molten baths containing the dopant to be introduced in the glass matrix. Transition metals such as Ag and Cu penetrate into the glass substituting the alkali species (typically the mobile Na) of the matrix. Recently, ion exchange techniques that exploit an external electric field to assist the migration have been developed: in this configuration, a metallic film is used as the metal dopant supplier, directly deposited on the glass matrix. Ion exchange in this case does not occur by interdiffusion between the dopant metal and the alkali ionic species, but by the simple occupation by the metal ions -coming from the film- of the alkali sites of the glass matrix. By the field-assisted configuration, it has been possible to perform ion exchange with multivalent ions such as Cu^{2+}, Co^{2+} [11], and Au^{3+} [32], driven by the gradient in the electrochemical potential.

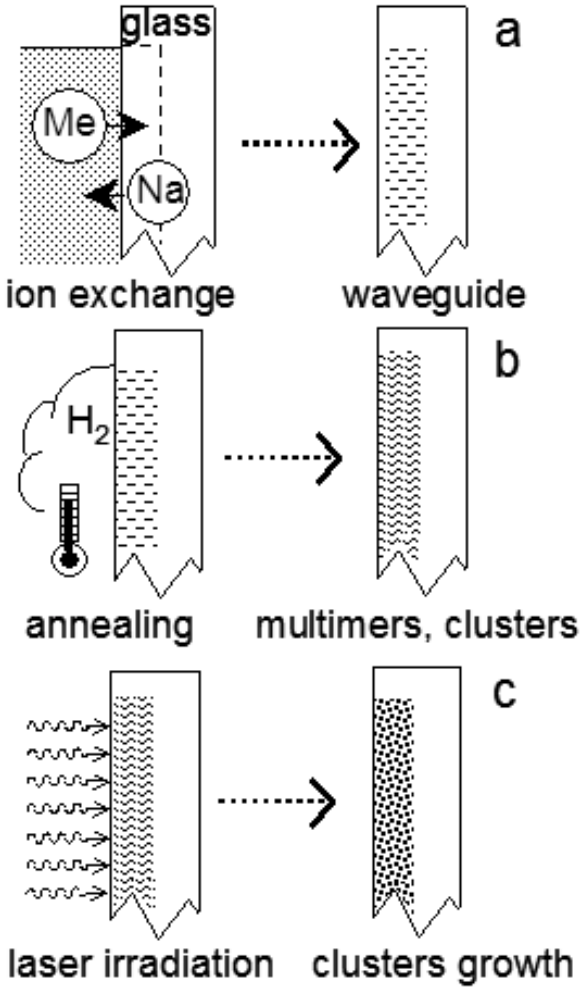

Fig. 8. Sequential treatments of ion exchange (a), annealing in selected atmosphere (b) and laser irradiation (c) for the control of nanocluster formation in glass.

The scheme in Fig. 8 illustrates a typical recent combined methodology, based on ion exchange, for metal nanocluster glass preparation. Dopant metal is first introduced in a superficial region of the glass (of typical thickness up to several micrometers) by means of an ion exchange procedure. In this way, depending on the metal, an optical waveguide may be formed, in which high metal concentration values can be reached without precipitation. Suitable annealing treatments then promote the aggregation of dimers, multimers and eventually very small nanoclusters, throughout the

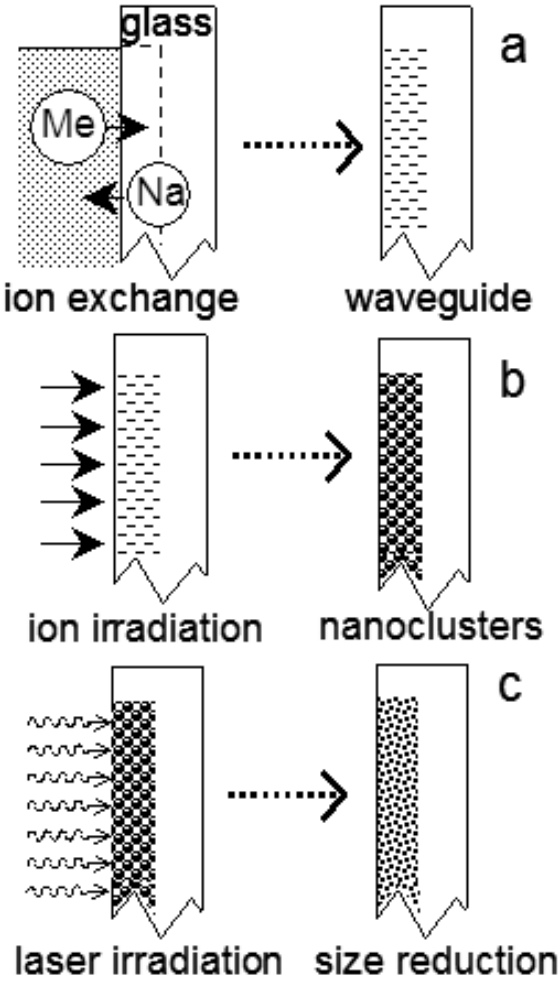

Fig. 9. Sequential treatments of ion exchange (a), ion irradiation (b) and laser irradiation (c) for the control of nanocluster formation in glass.

whole exchanged region. A further cluster growth may be then obtained by means of proper laser treatments, by which it is possible to form spherical nanoparticles homogeneous in size. Various experiments were carried out exploring the interaction between laser beams and metal-doped composite glasses [12,14]. Laser beams from either excimer (KrF) or Nd:YAG sources allowed to irradiate samples doped with silver or copper at different wavelengths, ranging from 248 nm to 1064 nm, so covering both the surface plasmon resonance and the off-resonance regions of the spectrum. By varying the laser wavelength and the energy density deposition range of the laser pulses, up to few J/cm^2, quite different structures were observed: metal nanoclusters of few nanometer size form in ion exchanged systems, while photofragmentation phenomena occur where bigger cluster are already present in the glass. The physical mechanisms involved in the observed phenomena are still to be investigated, as well as the role of the treatment parameters, with the aim to tailor the cluster formation and size in the glass by proper laser beam treatments.

In the case of silver-sodium ion exchanged systems [31], a further degree of freedom for controlling the final composite structure is given by the concentration of $AgNO_3$ in the $AgNO_3$:$NaNO_3$ molten salt bath in which the glass is immersed for the exchange process. At high silver nitrate concentration in the bath, the glass results to be doped at very high Ag concentration values, namely, up to several 10^{21} atoms/cm^3, i.e., well beyond the solubility limit of silver in glass even without precipitation. In this case, silver atoms do not simply substitute alkali (typically sodium) ions in ionic-type sites. Instead, a local Ag_2O configuration is observed (again from EXAFS measurements) in the site environment. Subsequent annealings in different atmospheres determine different behaviors, in which for example the cluster nucleation comes from the formation of $(Ag_3)^{2+}$ trimers in the case of annealing in air, while annealing in reducing atmosphere gives rise to high concentrated nanoclusters of somewhat bigger size [31].

Fig. 9 shows another sequence of treatments for the control of nanocluster formation in glass, based on the ion exchange process as the first step. In this case, a combination of ion and laser irradiation can be used to tailor the cluster growth and type. In particular, ion irradiation with light ions (typically H^+ or He^+) is used to promote the aggregation of relatively big clusters, of diameter up to 10 nm, homogeneous in size and distribution, owing to the energy deposited via electronic interaction by the ions of the beam.

It should be remarked that the ion exchange has demonstrated to be particularly promising where there is the need to control the homogeneity and the dopant metal concentration in relatively thick layers. This is for example the case of experiments involving rare earths doped glasses, for example with erbium, in which the presence of transition metals near the erbium atoms is quite effective for the enhancement of the luminescence properties of the glass, due to the optical emission of Er^{3+} ions at 1540 nm. By using, for example, suitable prepared glasses in the form of Na:SiO_2 sol-gel layers [3], one can control the number of sites available for the metal to be introduced in the glass by the ion exchange. This procedure allows to se-

lect the most proper distance between the metal and the rare earth atoms as well as the local glass composition, while the sequential treatments described above give an effective control on the cluster aggregation near the rare earth sites.

4. DISCUSSION AND CONCLUSIONS

Among the methods of synthesis and manipulation of glasses containing metal nanoclusters, those based on the use of ion beams are actually much interesting for their intrinsic flexibility and for the availability of several parameters for the control of the properties of the resulting material. In the case of ion implantation technique, the use of sequential implants of different ion species have demonstrated to promote the formation of a great variety of systems. Being an intrinsic out-of-equilibrium synthesis method, ion implantation allows the formation of stable systems with unique properties. Besides the technological parameters of implantation, that is, energy and dose of each ion beam, the choice of the implant temporal sequence and the relative doses of the two implanted species trigger the formation of cluster that may differ in size, composition and structure, presenting for example either alloy or core-shell structures. The use of subsequent sequential annealing treatments in selected atmosphere adds further degrees of freedom in the definition of the final cluster structures, and this allows to synthesize composites exhibiting a great variety of peculiar optical features, as evidenced by nonlinear optical measurements. Besides direct ion implantation of metal species, the irradiation of metal-containing glasses with light ion beams has demonstrated to effectively promote either the nucleation of nanosized cluster or its growth in size, in the case of already present aggregates. In fact, the most interesting feature obtained using light ion irradiation is the homogeneity of the cluster size throughout the whole doped region of the glass.

The ion exchange process is used to dope silicate glass matrices with metal concentration values beyond the solubility limits. This fact allows to control the nucleation and grow of metal nanoaggregates for a large range of volume fraction values, involving again both annealing in selected atmosphere and ion or laser irradiation. But the most interesting and potentially useful advantage in using the ion exchange technique is the possibility of operating subsequent treatments directly in light waveguiding layers, created by the high polarizability of the metal introduced in the glass by the exchange process. The ion exchanged based methods for the synthesis of nanostructured glass composites allow therefore -at least in principle- to comply with one important technological issue for the application of the composite materials in actual photonic devices, that is, the assembling in light waveguiding components. In our case, the clusterization is promoted directly in a substrate which may be designed for the final integrated components. Furthermore, ion or laser irradiation techniques able to tailor the cluster structures may be performed with a proper masking of the ion exchanged glass, so obtaining a direct patterning of the system, useful for integrated components design. This features may have particular importance in the telecommunication technologies involving the matching between glass-based amplification stages and optical fiber components. These systems, in which glass composites containing both metal nanoclusters and rare earth dopants are present, are the object of increasing interest, from the points of view of both the fabrication methods and the theoretical studies for the description of their behavior.

In general, for metal nanocluster composite glasses, the link between the observed features and the theoretical and phenomenological description of the phenomena is however far from being assessed in all its aspects. An exhaustive description of the nanocluster composite in terms of cluster nucleation and growth and in terms of size, size distribution, structure and stability will require an even more extended experimental work, in which to investigate the role played by the several parameters involved. In this respect, it is worth remarking the need for sensitive analytical techniques in the experimental investigation of the systems at issue, such as the techniques based on the use of synchrotron radiation. Considering the body of several works quoted in this paper, synchrotron radiation based allowed an insight about the composite glass structuring that could not be achieved by other conventional techniques: due to system dilution (metals are present at concentration values down to 10^{16} atoms/cm^2), an intense X-ray flux is needed such those available from synchrotron facilities. This allows also to perform both X-ray diffraction and X-ray absorption experiments in grazing incidence configuration, so obtaining depth-sensitive information by varying the incidence angle of the X-ray beam on the sample. Diffraction can detect crystalline structures of small size (of the order of few nm) present in thin layers (of the order of hun-

dreds of nm) such those obtained by ion implantation. On the other hand, EXAFS experiments can detect interatomic distances down to few thousandths of nanometer, as well as the nature of the chemical environment of the atomic species implanted [17,23] or introduced in the glass by ion exchange [10,11]. In particular, in the case of annealed systems, the clusterization of the dopant depends strongly on the different annealing atmosphere. Synchrotron based analyses help here [25,31] to answer here the question whether and how the aggregation comes to depend on the state of metal after the introduction (by either implantation or ion exchange), and how the atmosphere plays a role in the presence of different structures (i.e. clusters, dispersed atoms, oxide or metallic phases). In the case of ion exchanged systems, the knowledge of the metal site as a function of the depth is used to relate the local chemistry and concentration to the activation energy for ion diffusion between two adjacent sites: this activation energy, which enters in the diffusion model, is linked to both the neighbors atoms and the interatomic distances, due to the modification of the local network structure. Besides the understanding of the phenomena involved in the synthesis process, the general purpose is also to relate the observed behaviors to the treatment parameters, with the aim of establishing effective protocols for nanocomposites formation.

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