**Peculiarities and application perspectives
of metal-ion implants in glasses**

P. Mazzoldi^(a), G.W. Arnold^(b), G. Battaglin^(c), R. Bertoncello^(d),
F. Gonella^(a)

- (a) Unita' del Consorzio Interuniversitario Nazionale per la Fisica della Materia, Dipartimento di Fisica, via Marzolo 8, 35131 Padova, Italy
- (b) Sandia National Laboratories, Dept 1111, P.O. Box 58000, Albuquerque, NM 87185, USA
- (c) Unita' del Consorzio Interuniversitario Nazionale per la Fisica della Materia, Dipartimento di Chimica Fisica, Calle Larga Santa Marta 2137, 30123 Venezia, Italy
- (d) Dipartimento di Chimica Inorganica, Metallorganica e Analitica, via Loredan 4, 35131 Padova, Italy

Ion implantation in insulators causes modifications in the refractive-index as a result of radiation damage, phase separation, or compound formation. As a consequence, light waveguides may be formed with interesting applications in the field of optoelectronics. Recently implantation of metals ions (e.g. silver, copper, gold, lead,...) showed the possibility of small radii colloidal particles formation, in a thin surface layer of the glass substrate. These particles exhibit an electron plasmon resonance which depends on the optical constants of the implanted metal and on the refractive-index of the glass host. The non-linear optical properties of such colloids, in particular the enhancement of optical Kerr susceptibility, suggest that the ion implantation technique may play an important role for the production of all-optical switching devices. In this paper an analysis of the state-of-the-art of the research in this field will be presented in the framework of ion implantation in glass physics and chemistry.

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

1. Introduction

Ion implantation in insulators attracted a large interest in the last ten years, as shown, in particular, by the increasing numbers of papers in chemistry and physics journals, the presentation of specific papers in meetings and conferences, the high content level and the number of contributions at the 7th "Radiation Effects in Insulators" conference, which is held in Japan this year.

The interaction between incident ions and substrates causes effects directly connected to radiation damage, such as mechanical stresses, density and composition modifications, and consequent optical property changes. In addition to these, it is possible to form new compounds (chemical interaction), which originate in regions with very large differences in the refractive-index with respect to the substrate [1-7].

Recent papers dealing with the double implantation of nitrogen and silicon in silica glasses emphasized the importance of chemical interaction in determining the final properties of the implanted layers [8-14]. Silicon oxynitrides are formed with a modification of refractive-index and a decrease of etching rate in diluted HF solution [15].

The implantation of metals ions is of a particular interest: depending on their reactivity with the substrate, metal colloids or compounds can be formed.

Titanium silicide and titanium oxide compounds are observed, for instance, in titanium implanted silica, whereas tungsten implantation causes the formation of metallic tungsten precipitates and the presence of tungsten oxides. A subsequent nitrogen implantation destroys the titanium silicide species inducing the formation of titanium metallic clusters and substoichiometric silicon nitrides and transforms titanium oxides to

titanium oxynitrides. The nitrogen implantation in tungsten-preimplanted silica determines the formation of tungsten oxynitrides. These chemical interactions between the implanted species and the silica substrate have been interpreted on the basis of thermodynamic considerations [16-19].

On the other hand, implants of ions such as gold, silver, lead, copper and phosphorous induce the formation of colloids [1-2] which are of particular interest in non-linear optics applications. In fact metal colloids can yield an enhanced third-order susceptibility which leads to an intensity-dependent refractive-index [20-25].

In this paper we shall present an analysis of chemical interactions between implanted species and substrate, quoting some recent results, obtained by our group at the University of Padova, on silicon, titanium and tungsten implants in silica glasses. Effects of a subsequent nitrogen implantation are considered also.

After some general considerations on the non-linear optical field, a general review on the colloid formation as a consequence of metal-ion implants will be introduced and discussed in terms of non-linear optical glass (NLOG) materials perspectives of application.

2. Chemical interactions

The Padova group studied silica glasses implanted with titanium or tungsten ions using X-ray photoelectron spectroscopy (XPS), secondary ion mass spectrometry (SIMS), Rutherford backscattering spectrometry (RBS) and nuclear reaction analysis (NRA) [17-19].

Implants of titanium in silica, aside from the radiation damage to the substrate, introduce a very reactive element in a chemically stable matrix. Formation of titanium silicides is expected, for instance, on the basis of the

observed chemical reaction between thin refractory metal films and SiO₂ substrates under thermal anneal in vacuum. According to thermodynamic considerations, the following reaction is allowed:

The formation of pure metallic species according to the reaction:

is thermodynamically less favourable with respect to titanium silicides. In fact the ΔG°_{298} values for the formation of both TiSi and Ti₅Si₃ species (reaction 1) are $\Delta G^\circ_{298}(\text{TiSi}) = -1021$ kJ/mole and $\Delta G^\circ_{298}(\text{Ti}_5\text{Si}_3) = -2194$ kJ/mole respectively to compare with the value of $\Delta G^\circ_{298} = -891$ kJ/mole for reaction 2 [26]. The formation of TiSi or Ti₅Si₃ is also expected to depend on the titanium local concentration.

In the case of a silica sample implanted with 30 keV, 5×10^{16} titanium ions/cm², the XPS spectrum of the unresolved Si(2p_{3/2+1/2}) doublet, at different depth from the surface up to a depth of about twice the mean projected range ($R_p=32\text{nm}$), is reported in Figure 1. The spectrum shows two distinct components; one of them is centred at a Binding Energy (BE) of 103.7 eV, corresponding to the silica matrix, and the other at 99.4 eV, consistent with the presence of titanium silicide.

The Ti(2p) spectrum, reported in Figure 2 for a depth close to R_p , confirms the previous analysis. It is the envelope of two doublets whose 3/2 components are centred at a BE of 458.3 eV, ascribed to Ti-O bonds formation, and at a BE of 454.3 eV, due to titanium silicide.

The O(1s) peak presented a main component at a BE of 532.7 eV, related to silica and a shoulder at a lower BE (531.1 eV), which may be ascribed to the substitution of silicon by titanium in the silica tetrahedron with the formation of Si-O-Ti bonds. This assignement was confirmed by the presence in the IR-Diffuse Reflectance spectrum of a characteristic band (at about 940 cm^{-1}), attributed to tetra-coordinated titanium atoms in mixed $\text{TiO}_2\text{-SiO}_2$ systems.

Tungsten is less reactive with silica than titanium. It is known that tungsten can form clusters and oxides structurally disordered with metallic centres chemically inequivalent.

Thermodynamic considerations applied to the system silica implanted with tungsten suggest that silicide specie formation is less favoured than the simple formation of tungsten metallic precipitates.

The ΔG^0_{298} values for the two reactions:

are $\Delta G^0_{298} = -1806\text{ kJ/mole}$, for reaction 3, and $\Delta G^0_{298} = -2361\text{ kJ/mole}$, for reaction 4, respectively .

The $\text{W}(4f_{7/2})$ XPS peak of 200 keV , $5 \times 10^{16}\text{ cm}^{-2}$, tungsten-implanted silica is reported in Figure 3. The line peak, at a depth close to R_p (75 nm), has been deconvoluted into three distinct doublets whose $4f_{7/2}$ components are centred at 32.0, 33.4 and 37.4 eV respectively. The lower BE component has been assigned to metallic precipitates because no silicide signal has been detected in the corresponding $\text{Si}(2p_{3/2+1/2})$ line. The component at 33.4 eV must be associated with the presence of tungsten oxides as confirmed by

the presence of a low BE component at 530.8 eV in the O(1s) line. The higher BE peak can originate from the interaction between the tungsten oxides and silicon dioxide.

Nitrogen implants were made in the silica glasses preimplanted with silicon, titanium or tungsten. A strong chemical interaction between nitrogen and the implanted metal is evident by observing Figure 4, where the depth profiles of nitrogen (100 keV, 2×10^{17} ions/cm²) implanted in silica and in silicon (a), titanium (b) and tungsten (c) preimplanted silica. The depth profiles of the metal ions are also reported.

In pure silica the depth profile of the implanted nitrogen is flat, extends to much greater depths than the calculated R_p [27,28] and the average stoichiometry of the SiO_xN_y compound formed is limited by the redistribution of nitrogen ions during irradiations [8]. The nitrogen profile is very different if its implantation is made into silicon, titanium or tungsten preimplanted silica. The nitrogen distribution in this case follows the profile of the metallic implanted species, indicating that a chemical interaction took place. In the case of silicon preimplanted silica, an increase of the retained nitrogen concentration is also observed and is connected to a change of the SiO_xN_y compound stoichiometry.

Large modifications are induced by nitrogen implantation in titanium preimplanted silica. The Ti(2p) signal close to R_p shows a broad envelope constituted of two doublets whose 3/2 components are centred at BE values of 455.4 and of 453.0 eV. The higher BE signal indicates the presence of titanium oxynitrides, confirmed by a corresponding contribution present in the N(1s) signal. The lower BE contribution to the Ti(2p_{3/2}) peak can be attributed to the formation of metallic clusters. The formation of titanium oxynitrides, substoichiometric silicon nitrides (and not silicon oxynitrides)

and N_2 molecules, trapped in the silica matrix, are evidenced by the analysis of $N(1s)$, $O(1s)$ and $Si(2p_{3/2+1/2})$ signals.

These results can be described by the following reactions:

In the case of the tungsten-preimplanted sample, the nitrogen implantation induces the formation of tungsten oxynitrides. The quantitative analysis of the whole set of signals is consistent with the presence of metallic tungsten, WO_xN_y and mixed $WO_x \cdot SiO_2$ dispersed in the silica matrix.

In the $Ti-SiO_2$ system the chemical effects play the major role taking into account that ΔG°_{298} for SiO_2 and TiO_2 are comparable. On the other hand, in the tungsten- SiO_2 system, WO_2 and WO_3 are much less favoured than SiO_2 and the ballistic effects dominate.

We want to observe that the introduction of thermodynamic considerations in order to explain the chemical interactions between implanted species and the substrate presents some uncertainty, due to the correct values of the local temperature and, consequently, of ΔG° . Moreover it is necessary to ascertain if the interaction is between the implanted ion and the separate atomic species of the substrate or between the implanted ion and the substrate atomic groups. The ΔG° values may be very different in the two cases.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

3. Non-linear properties of metal-doped glasses

3.1. Background

Optical non-linearity of glasses results mainly from three effects: thermal effect, electrostriction and non-linear polarization [29]. The first two effects depend on the changes in the density and polarizability due to thermal and electric fields, respectively, while the latter is connected with the non-linear distortion of the electron orbits surrounding the average position of the nucleus. The relative contribution of each effect to the non-linear response will depend, in turn, on the time scale of the pulse duration of the laser beam. Non-linearity in glasses is in general quite small, but the non-linear response may be enhanced of several orders of magnitude by introducing small metal clusters: the non-linear properties of metal clusters embedded in a dielectric matrix has been studied mostly in the case of gold [30 and references therein, 31-33], titanium, copper, lead and bismuth [34-36]. Also in the case of silver a considerable amount of literature can be found concerning the role played by the metal clusters in giving rise to non-linear effects [20 and references therein].

The non-linearity in metal doped-glasses is mostly due to third-order processes described by the real part of the third-order electric susceptibility, $\chi^{(3)}$, involving different four-wave mixing processes [37]. A particular four-wave mixing process in which all the frequencies involved are the same is referred to as the optical Kerr effect, which is the most important for the applications in all-optical switching devices [23].

The origin of this non-linear response may be ascribed, in the case of small metal particles, to the intraband, direct interband and hot electron transitions [32].

The third-order term originated from the conduction electrons is described quantum mechanically by the quantum size effect [38]. Non-linear responses in the 5-ps time scale have been observed and described in terms of quantum size effect firstly by Hache and co-workers [39]. The confinement of the conduction electrons, which can be classically described in terms of limited mean free path, gives rise to an expression for $\chi^{(3)}$ varying roughly as a^{-3} if a is the radius of the metal sphere.

Interband transitions between the d -levels and the conduction band also contribute to the non-linear response of a metal-doped glass. This process is a resonant and size-independent one, corresponding to the saturation of the two-level transition between the bands.

A third contribution has been described and quantitatively evaluated for gold [39]. It is ascribed to the hot electrons created by the strong absorption near the surface plasmon resonance, which, in turn, depends on the particle size, leading to a modification of the absorption coefficient of d -electrons. In the case of gold particles, the dominant contributions are those from the hot electrons and the interband transitions, while in the case of silver the interband contribution is expected to be the major one [32].

In addition, an effective-medium theory approach [33] relates the third-order susceptibility of metal clusters embedded in a linear dielectric medium to the composite effective susceptibility by a local-field enhancement factor. Moreover it is worth noting that anisotropy relationships [32,39] exist among the components of the fourth-rank tensor $\chi^{(3)}$. In particular, Magruder and co-workers [30] point out the different role played by the $\chi^{(3)}_{xxxx}$ and $\chi^{(3)}_{xxyy}$ components. $\chi^{(3)}_{xxxx}$ can include contributions from both thermal and electronic processes, while the $\chi^{(3)}_{xxyy}$ component is related only to electronic ones.

Four-wave mixing refers to non-linear processes with four interacting electromagnetic waves. It is a third-order process governed by the third-order non-linear electric susceptibility. Owing to the inversion symmetry properties of glasses, third-order non-linearity is the lowest-order non-linearity allowed under the electric-dipole approximation [40].

3.2. *Experimental*

The non-linear properties of metal-doped glasses can be measured by several techniques, among which are the degenerate four-wave mixing methods [30-32], and the so-called Z-scan method [34-36].

When all the four waves involved in the four-wave mixing process have the same frequency, one talks about degenerate four-wave mixing (DFWM). In Figure 5 the forward- and the backward-mixing arrangements are shown, respectively. In the former case there are two input beams, the pump and the probe, while in the latter there is also a backward pump beam, usually obtained by a mirror placed beyond the non-linear medium. In both cases, the non-linear polarization radiates a signal field at ω in the phase-matched direction. A physical interpretation of the process can be given in terms of grating formation in the non-linear medium: the pump and the probe waves interfere giving rise both to amplitude gratings (resulting from the non-linear loss due to two-photon absorption) and refractive-index or phase gratings (due to the intensity-dependent refractive-index change), from which the waves scatter coherently. The output intensities of signal and probe are related to the non-linear absorption and to the non-linear gain, from which one can determine the third-order term $\chi^{(3)}(-\omega; \omega, -\omega, \omega)$, which can be in turn related to the non-linear refractive-index n_2 .

More recently, the Z-scan method [41] has been exploited for direct measurements of n_2 . In this configuration, the light intensity transmitted across the non-linear material is measured through a finite aperture in the far field as the sample is moved along the direction of propagation (z-axis) of a focused Gaussian laser beam. Figure 6 illustrates the principle of the method, that has the advantages of using a single beam, and allows the magnitude and the sign of the non-linear refraction to be obtained.

When the sample moves towards the focus from negative z , the power density increases, giving rise to self-focussing [40]: owing to the Gaussian transverse intensity profile of the laser beam, the original plane wavefront of the beam gets progressively more distorted, in a way similar to that imposed by a positive lens, leading to a self-focussing that shifts the position of the actual focal point, since the ray propagation must be perpendicular to the wavefront. A displacement of the focal point towards negative z gives rise to an increased divergence of the output beam, and thus to a decrease in the intensity at the detector. For positive values of the z position of the sample, the same effect gives rise to a decreased divergence, that is, to an increased intensity at the detector. When the sample is at $z=0$ the self-focussing does not affect the output. The same occurs when the sample is far from the focal point, since the power density is low and self-focusing effect is negligible. It is worth noting that the intensity change due to absorption effects can be evaluated by removing the aperture in front of the detector. The difference between the peak and the valley in the output intensity figure is proportional to the phase distortion of the beam, which is, in turn, related to the non-linear refractive-index, n_2 .

3.3. Applications

Non-linear optical glass materials are attractive in the field of optoelectronics owing to the high transparency, ease of fabrication, durability and stability. In particular, much attention is paid to the possibility of fabricating all-optical switching devices based on the non-linear properties of glasses containing metallic nanoclusters. The capability of processing light signals without converting them to electronic form should allow all-optical devices to operate in a time range inaccessible to electronics. The fastest electronic components can operate in the picosecond range, while light pulses can be generated in the femtosecond range. Furthermore, all-optical switches are the base for developing optical parallel data processing systems and optical time domain multiplexing transmission systems [21].

Non-linear switching devices are based on optical waveguiding structures for they provide strong beam confinement in prescribed patterns [42]. In these devices, the intensity of an optical signal is used as the parameter that causes switching between two output channels that performs logic operations.

In Figure 7 two typical examples of all-optical devices are illustrated, together with their response to optical power without (dashed lines) and with (solid lines) non-linearity.

It is worth noting that the production of non-linear optical devices requires patterning the layer or circuit with the prescribed properties, and that ion implantation is one of the suitable methods for this purpose, considering that the distribution and the concentration of dopants can be controlled.

4. Cluster formation

Cluster formation in metal ion implanted silica and glasses has been studied by using different techniques. Optical absorption measurements and transmission electron microscopy (TEM) give informations on cluster shape and size and crystalline state. RBS has been used to obtain the implanted ion depth distribution. XPS and Auger electron spectroscopy (AES) determine the chemical state of the implanted ions. Complementary information is given by electron paramagnetic resonance (EPR) and infrared reflectance measurements

The Z-scan technique and the DFWM method have been used for measurements of the third order susceptibility, $\chi^{(3)}$.

4.1. Copper implants

Copper implantation in glasses was mainly studied by groups of the Vanderbilt University (and Oak Ridge Labs.) [34-36,43,44] and the Nagoya Institute of Technology (and the University of Nagoya) [45-47].

In copper-implanted silica glasses a peak in the optical absorption spectra appears at 2.2 eV (532 nm). Two copper-related colloids give rise to an absorption band centred around 2.2 eV: metallic copper [48,49] or cuprous oxide [50,51]. The absorption in metallic copper particles is due to the copper surface plasma resonance, while in cuprous oxide particles is due to an excitonic transition. The temperature dependence of the two types of transitions is quite different: absorption due to plasma oscillations is not expected to depend on the temperature, while the widths of absorptions due to excitons decrease remarkably with decreasing temperature [50,51]. No changes were observed in the absorption spectra of 160 keV copper-

implanted silica, at a fluence of 6×10^{16} ions/cm², between 300 and 77 K, indicating that the peak at 2.2 eV should be attributed to metal copper particles [46].

Direct evidence for the formation of copper colloids has been obtained by TEM. The observation of samples in a direction parallel to implanted layers [47] showed that the particle diameters, almost constant at a given depth, vary with depth in the range 2-8 nm. All the observed electron diffraction rings can be indexed as arising from crystalline copper.

The RBS measurements of the copper profiles showed a near-Gaussian distribution for fluences lower than 2×10^{16} ions/cm² and a bimodal distribution for fluences higher than 3×10^{16} ions/cm² [43,44,47] (Figure 8). The larger peak in the bimodal distribution is approximately twice the size of the smaller and nearer to the surface.

Changes in the fluence rate for fluences greater than 3×10^{16} ions/cm² modify the optical absorption at 2.2 eV without affecting the spatial distribution of copper ions. It is believed that the observed modification (a non-linear increase in absorption with increasing fluence rate) is due to alteration of the shape of the colloids from spherical to prolate spheroids [43]. The relation between the shapes of copper concentration, in-depth distribution and particle diameters is reported in Figure 8. The distribution of particle diameters is close to the distribution of copper concentration: the diameter of metallic copper colloids increases, in a first approximation, linearly with the copper concentration. The bimodal distribution of the implanted copper has been observed also for silver implants (see in the following). The interpretation of the phenomenon is open; certainly the diffusivity of the implanted species, the deposited energy distribution and defect migration would play an important role in the determining the final concentration profile of colloids.

Modifications of size and shape of copper colloids has been obtained by a subsequent fluorine ion implantation in copper-implanted silica samples [55]. After the fluorine implantation, the position of the absorption peak corresponding to plasma oscillation (2.2 eV) is shifted to 2.1 eV (591nm). This is interpreted in terms of a coalescence of copper particles to form larger colloids with nonspherical shape. Such interpretation has been confirmed by TEM observation: particles with nonspherical shape became prominent, the particle size increased approximately of a factor 2. The distribution of copper remained bimodal in shape, but both distributions narrowed. Hosono *et al.* [45] suggested that the interaction between fluorine and copper is responsible for the coalescence mechanism. This phenomenon may be connected also to the electronic energy deposition due to fluorine implantation.

A bimodal distribution was observed also by G. W. Arnold *et al.* [52] and by the Padova group [53] in silver-implanted silica, where silver colloids are present. A correlation between the presence of metallic colloids and a bimodal distribution of the implanted element seems evident, but an explanation of this is not yet available.

Vanderbilt and Padova groups did not observe any absorption feature, connected to copper colloid formation, for borosilicate (Pyrex), aluminosilicate (Corning 0312), or for soda-lime glasses [54-56]. Such results are not in agreement with the interpretation [47] that the formation of metallic colloids for noble metals (such as gold, silver and copper) implantation may be understood by assuming a local high temperature as a consequence of collision cascades (thermal spike). In fact the implantation conditions are similar for experiments in silica, where colloids are evident, and in silicate glasses where colloids do not form. The straightforward conclusion is that the formation of metal colloids is mainly governed by the glass structure and composition. In any case, metal clusters, as dimers,

trimers and clusters smaller than about 1 nm, do not contribute to the surface plasmon resonance absorption, considering that the mean free path of the conduction electrons is strongly limited by the cluster size.

The Cu(2p_{3/2}) XPS peak for 90 keV, 5×10^{16} ions/cm², copper implanted silica (reported by the Padova group in another contribution to this conference [56]) shows a BE value of 932.7 eV, the same value measured for a bulk copper sample. An inspection of the Cu_LVV AES signal confirms the presence of metallic copper: its kinetic energy (KE) value is 918.2 eV for copper-implanted silica, again equal to the value measured for bulk copper. Quite surprisingly the KE value of 917.6 eV was found for a copper-implanted soda-lime glass, even though no absorption due to colloids was observed for this sample. This result can be explained by the fact that copper aggregates in the implanted soda-lime glass exist, but have diameters much smaller than 1 nm. The dissolution of copper clusters has been obtained by implantation of nitrogen in copper-preimplanted silica: the optical absorption peak (2.2 eV) disappears, the BE of the Cu(2p_{3/2}) peak assumes the value of 933.4 eV and the KE of the Cu_LVV AES signal becomes 913.9 eV, a typical value for copper in oxidised state.

The non-linear index, n_2 , of 160 keV copper-implanted silica, at a fluence of 10^{17} ions/cm², was determined by the Vanderbilt group using the Z-scan method [36]. The light source was a cavity-dumped dye laser with a pulse duration of 5.5 ps, a 3.8 MHz pulse repetition rate, 100 mW average power, and a peak irradiance of the order of 5×10^8 W/cm². Over the frequency range from 600 to 570 nm, the authors found that $2.0 \times 10^{-10} \leq n_2 \leq 4.2 \times 10^{-10}$ cm²/W.

Figure 9 shows $\chi^{(3)}$ as a function of wavelength near the 2.2 eV peak in the optical absorption spectrum, computed from the n_2 . The apparent maximum in $\chi^{(3)}$ suggests that the excitation of the surface plasmon

resonance contributes to the non-linear response. The main contribution to the electronic non-linearity near the surface plasmon resonance is attributed to photoexcitation of electrons in the conduction band, but interband contributions from the excitation out of the d band to the s - p conduction band states near the Fermi energy are also expected.

The magnitude of $\chi^{(3)}$ is of order of 10^{-8} esu, much smaller than the thermo-optic non-linear susceptibility of about 10^{-6} esu reported for longer FWHM laser pulses, 100 ps, at 532 nm [35]. Such difference is consistent with the different pulse lengths, 5.5 ps to compare with 100 ps: for short pulse length fast electronic effects are the principal contributors to $\chi^{(3)}$, whereas for longer pulses the high absorption, about 10^4 cm $^{-1}$, leads to thermal self-focusing.

4.2. Silver implants

In this case the most detailed analysis was made by G.W. Arnold and co-workers and by our group [52,53,55,57,58]

Recently [53], optical and RBS techniques have been used to determine the size and spatial distribution of implanted silver (270 keV, 1.5×10^{16} ions/cm 2 , at low current density and room temperature) in dispersed and colloidal form in glasses of different composition. The glass types and their adopted acronyms were: Corning 7940 fused silica (CFS), the borosilicate Pyrex (PYR), a simple alkali-borosilicate (5% K $_2$ O, 20% B $_2$ O $_3$, 75% SiO $_2$) (BSG) and a soda-lime glass (SLG). Half of each sample was also implanted with 100 keV nitrogen ions to the fluence of 1.5×10^{17} ions/cm 2 . Specimens were also subjected to isochronal (30 minutes) annealing, in air, at temperatures in the 200-700 °C range. The distribution and size of colloidal silver particles in unannealed samples was studied in detail. In Figure 10

we report the RBS spectra for CFS, PYR and SLG silver-implanted samples and in Figure 11 the RBS spectra for the same samples after the further nitrogen irradiation. The depth and concentration scales for silver are shown.

Optical absorption spectra (not reported) show an absorption band, centred at 395~415 nm (3.1~3.0 eV), characteristic of silver colloids for all samples, except silver-implanted SLG. Absorption curves were fitted in the framework of the Mie theory [59] and colloid radii were calculated.

The distribution and size of the particles clearly depend on the substrate type, in particular in CFS the distribution looks bimodal with the two contributions centred at the depth at which the maximum damage occurs (93 nm) and at R_p (129 nm). An appreciable fraction of the implanted silver precipitated to form colloids of 1.5 nm radius, probably in the middle of the distribution. Borosilicate glasses (PYR and BSG) behave qualitatively similarly one to the other, showing a drift towards the surface of the implanted ions, probably due to a stress field. At the surface, a small fraction of implanted silver precipitates and forms colloids of 1.5 and 1.2 nm radius for PYR and CFS, respectively.

A TEM analysis of the silver-implanted CFS sample showed a large number of crystalline silver precipitates, with the radii distribution reported in Figure 12. The good agreement between the calculated colloid radii, using the optical absorption data, and the measured values is evident.

The implantation of nitrogen ions causes a migration of silver atoms. It results in large modifications of silver concentration profiles and increase in size and reduction in number of colloids. Silver colloids are now present also in SLG. As a consequence of the nitrogen irradiation, colloid radii became 2.0, 2.4, 1.8 and 1.9 nm for CFS, PYR, BSG and SLG, respectively.

Results of the XPS analysis of CFS and SLG are very similar. For both samples, at a depth close to R_p , the $\text{Ag}(3d_{5/2})$ peak is centred at a BE of 368.5 eV; the same component for metallic silver takes a BE value of 368.2 eV. On the other hand the BE values of the silver oxides range close to the values reported for the metallic specie so that no unambiguous evidence of the silver oxidation state can be obtained from the XPS analysis. However, from literature data [60], the silver $M_{5N_{45}}N_{45}$ AES signal for the metallic and oxide species is shifted by 1.1 eV and the corresponding α parameter ($\text{Ag}(3d_{5/2})\text{BE} + \text{Ag}(\text{MNN})\text{KE}$) takes the value of 726.1 for metallic silver and ranges from 724.0 to 724.5 eV for silver oxides. In our samples the α parameter for Ag at depths close to R_p , takes a value of 725.7 eV. This is a clear indication that silver is embedded in the silica matrix in form of small metallic precipitates. As in the case for copper, silver colloids in silver-implanted SLG should be constituted by aggregates of few atoms, in which a surface plasmon resonance cannot establish. After the nitrogen irradiation no indication of chemical interactions between silver and nitrogen is present, the $\text{Ag}(3d_{5/2})$ peak still shows a single component at a BE of 368.5 eV, with an about 0.4 eV narrowing of the FWHM indicating a more homogeneous size distribution of the silver precipitates.

Annealing effects are different for CFS with respect to the other glasses: in CFS colloids increase in size (at 700 °C the colloid radii are 3.3-3.4 nm for both the silver- and silver+nitrogen-implanted samples) and reduce in number, without appreciable dissolution in the substrate (at least below 700 °C). In the other glasses we observe a reduction, both in size and number, of colloids, with the eventual dissolution at 300-400 °C. This effect is less marked in silver+nitrogen-implanted samples. The cluster dissolution during the annealing process in PYR, BSG and SLG can be due to a sort of ion exchange between ionised (by oxidation) silver atoms from the colloids

and alkalis coming from the bulk of the glass. In fact we also observed a movement of alkalis to fill again the region from which they were depleted during the implantations.

From the above reported results it is clear that the increase in colloidal optical absorption after the nitrogen irradiation is not a purely thermal effect. It is mainly a phenomenon connected to the electronic energy deposition due to nitrogen implantation [57]. The conversion of the implanted silver to metallic colloidal form by electronic excitation and ionization processes has been well known from earlier studies of the effect in radiophotoluminescent silver-doped glasses [61].

$\chi^{(3)}$ values are not reported for silver implanted glasses. On the other hand, glasses containing silver clusters of about 2 nm in diameter [39,62] exhibit third-order optical non-linearities of the order of 2.4×10^{-9} esu. Samples with silver clusters produced by ion implantation should present higher $\chi^{(3)}$ values.

4.3. Lead implants

The Vanderbilt group studied this case [63,64].

Multicomponent glasses containing lead ions have been considered as candidates for fast photonic switching media [65]. In fact the local environment of the polarizable ions and the bonding arrangements may influence the non-linear response of such materials [66].

Silica samples were implanted with 320 keV lead ions, at fluences of 1, 3 and 6×10^{16} ions/cm². The higher fluence implanted sample was also annealed at 800 °C in air. The annealed profile showed a bimodal distribution (not present in the as-implanted sample) with a peak of maximum concentration at the depth of 80 nm and a second peak at 120 nm.

A decrease of about 30% in the lead concentration was observed after the annealing process.

Optical absorption spectra show a resolved but broad peak at about 5.2 eV for the sample implanted with a fluence of 1×10^{16} ions/cm². The other samples present a similar optical behaviour, but the peak at 5.2 eV becomes a broader shoulder that increases in magnitude with increasing fluence as does absorption throughout the rest of the spectrum. After the annealing the absorption spectrum exhibits a broad asymmetrical peak at about 5.4 eV. On the basis of literature data for various silicate glasses, containing different lead concentrations [67-69], Magruder *et al.* [63] attributed part of the absorption intensity of the broad shoulder at about 5.4 eV (in as-implanted samples and in the annealed one) to Pb²⁺ ions. Such interpretation has been confirmed in the observation of the Pb-O stretch in the far-IR. TEM analysis of the higher fluence, unannealed, sample showed the presence of elemental lead particles, with diameters less than 5 nm [64]. The expected surface plasmon resonance of lead particles embedded in silica is at about 3.5 eV [70]. The optical data do not evidence a feature that can be assigned to the surface plasmon resonance absorption of metallic lead particles. The authors claim that in the presence of a distribution of lead ions into different chemical states the plasmon surface resonance may be small. The relative fraction of the chemical states present in the samples depends on the implanted fluence, as observed for iron implantation in silica [71].

After annealing no evidence for elemental lead was found and the formation of lead silicate phase was evidenced by IR measurements. The remaining absorption centered at about 5.4 eV was again attributed to Pb²⁺ ions.

The as-implanted and annealed samples indicate the two extreme situation for the incorporation of metal lead particles or lead-silicate formation. The control of annealing temperature and the variation of the implantation parameters may modify the chemical properties of the lead implanted layer and its non-linear optical properties.

Haglund *et al.* [35] measured the non-linear refractive-index in lead-implanted silica using 100-ps pulses from a CW, mode locked, frequency doubled Nd-YAG laser. They found a value for n_2 of $3 \times 10^{-10} \text{ m}^2 \text{ W}^{-1}$, corresponding to a $\chi^{(3)}$ value of about 10^{-5} esu. Such a high value is due to thermal self-focussing connected to long laser pulses (see paragraph 4.1.).

4.4. Gold implants

The formation of gold colloidal particles (2-4 nm in diameter) in implanted lithia-alumina-silica glasses were observed by G.W. Arnold [72] to occur when the glass was heated near 550 °C. At that temperature the precipitation of the Li_2SiO_3 crystalline phase also occurred.

More recently, experiments have been performed in silica glasses by the Vanderbilt group [30]. Fused silica samples were implanted at room temperature with 2.75 MeV gold ions to a fluence of $1.5 \times 10^{17} \text{ ions/cm}^2$. Annealing of some specimens, in an atmosphere of Ar with 4% H_2 , for 2.2 h at 1100 °C (sample A), or in O_2 , for 5 h at 900 °C (sample B), was subsequently performed. Figure 13 shows the optical absorption for the three samples. The absorption increases with photon energy from 1.8 eV to 6.2 eV, showing, at about 2.4 eV, a slight inflection in as-implanted sample, a small broad peak in sample A and a well resolved peak in sample B. The peak in the absorption spectrum was attributed to the surface plasmon resonance of gold clusters. The clusters in as-implanted silica are

estimated to be less than 5nm in diameters, while clusters in the annealed samples have diameters in the 5-30 nm range.

$\chi^{(3)}$ values were measured by DFWM, using a mode-locked Q-switched, frequency-doubled Nd:YAG laser at a wavelength of 532 nm, near the surface plasmon resonance of gold (530 nm), with a pulse repetition frequency of 10 Hz and a nominal pulse width of 35 ± 5 ps. Maximum irradiance was always less than 10^9 W/cm², below the intensities for laser-induced thermal damage to the sample and for saturation in ruby-gold filter glasses [32,73]. The measured values of $\chi^{(3)}_{\text{xyy}}$, due to electronic processes, as intraband, interband and hot electron transitions, were 1.0×10^{-10} esu for the unannealed sample and 1.7×10^{-10} esu for sample A. It is interesting to compare these $\chi^{(3)}_{\text{xyy}}$ values to those obtained in filter glasses [32]: filter glasses with cluster diameters smaller than about 5 nm have $\chi^{(3)}_{\text{xyy}} = 6 \times 10^{-13}$ esu, while other with cluster diameters ranging than from 7 to 30 nm have $\chi^{(3)}_{\text{xyy}} = 1.4 \times 10^{-11}$ esu. The enhancement in the electronic component of $\chi^{(3)}$ after annealing is partially connected to the increased volume fraction of the nanoclusters in the silica-gold composite layer.

The experiments by Fukumi *et al.* [31] concerned silica glasses implanted with 1.5 MeV gold ions, at a fluence of 1×10^{17} ions/cm², and subsequently annealed for several hours at 700-900 °C. An absorption band due to the gold colloids was observed at about 532 nm. From its FWHM (82 nm = 0.32 eV) the average radius of the gold colloid particles was estimated to be about 2.9 nm. $\chi^{(3)}$ values were measured by using the DFWM technique, with a nominal pulse width of 7 ns, at a wavelength of 532 nm. The $\chi^{(3)}$ estimated value was 1.2×10^{-7} esu, very large when compared with that of gold colloid particles dispersed glass prepared by the melting method ($\chi^{(3)} = 10^{-11} - 10^{-13}$ esu) [32]. A comparison between the pulse laser duration, picoseconds in the experiment by Magruder *et al.* [30] and nanoseconds in

this one [31], leads one to connect the very large $\chi^{(3)}$ measured value with thermal effects, arising from the longer laser pulse duration.

4.5. Phosphorous implants

Hosono and co-workers [74,75] prepared nanocomposites of amorphous red phosphorous colloid particles and silica glass by ion implantation. Silica glasses were implanted with 180 keV phosphorous ions at nominal fluences of 6×10^{16} and 5×10^{17} ions/cm². At the lower fluence, the glass was colorless and XPS measurements showed only the formation of P-O bonds. However, for the higher fluence, the glass coloration was reddish-yellow and XPS showed that the major feature was the formation of P-P bonds, i.e. elemental phosphorous. Such results are in agreement with the previous investigations of Tagami *et al.* [9].

TEM measurements [74] showed colloids of 3-5 nm diameter. The electron diffraction pattern was that for an amorphous material. This result is in agreement with the fact that red phosphorous is quite difficult to crystallize and the conversion amorphous to crystalline occurs at high temperature, 400-580 °C, with an annealing for several tens of hours.

More complex behaviour is displayed for implantations in silicate glasses. Oyoshi *et al.* [76] found that the chemical interactions of the implanted phosphorous strongly depend on the glass composition and on the implanted ion fluence. Alkali depletion has been observed to govern the final state of the implanted ions.

$\chi^{(3)}$ values were measured by the DFWM technique using a two-beam configuration [75]. Specimens were excited with two beams of the excimer (XeCl)-pumped dye laser, with a pulse duration of 20 ns at a wave-length around 390 nm. A value for $\chi^{(3)}$ of 1.2×10^{-6} esu was determined. This

finding of a large third-order susceptibility for an amorphous semiconductor quantum dot leads the authors to speculate that amorphous red phosphorous has some intermediate order. The possibility that such measurements, performed using *nanosecond* lasers, are overwhelmingly dominated by the thermal component of $\chi^{(3)}$, needs a more in-depth analysis and measurements by using a ps-pulsed laser.

4.6. Tin implants

Silica glass substrates were implanted by Takeda *et al.* [77] with 400 keV tin ions to a fluence of 2×10^{17} ions/cm², at room temperature.

Metallic tin microcrystallites in the range 4-20 nm in diameters were observed by TEM.

$\chi^{(3)}$ value was obtained by DWFM, using two beams of a dye-laser with a pulse duration of 5 ns, at a wavelength of 500 nm, corresponding to the surface plasmon resonance of tin. The measured value was 3×10^{-6} esu, probably determined by thermal self-focusing effects, due to long pulse duration.

4.7. Iron implants

100 keV iron ions were implanted by Perez *et al.* [71] in silica glasses, at fluences ranging from 1×10^{16} to 2.5×10^{17} ions/cm². The Fe/Si ratio for the limiting fluences was 6% and 150 %. Conversion electron Mössbauer spectroscopy (CEMS) was employed. This technique is sensitive to as little as 10^{15} Fe/cm² and to a depth of about 200 nm. Fe⁰, Fe²⁺ and Fe³⁺ were detected. The metallic iron precipitates are lower than 4 nm for fluences up to 6×10^{16} ions/cm² and reach dimensions greater than 8 nm at a fluence of 1.4×10^{17}

ions/cm². Above 1×10^{17} ions/cm² the metallic fraction of the precipitates exceeds 50%.

CEMS measurements were performed also by Zhang *et al.* [78] in SiO₂ single crystals implanted with 60 keV iron at a fluence of 5×10^{16} ions/cm². Samples were annealed in a hydrogen atmosphere up to 700 °C. In this case TEM analysis showed metallic precipitates with an average size of about 25 nm.

5. Erbium implants

Erbium doping of optical fibers is now routinely used for amplifiers and lasers [79,80]. The incorporation of planar optical waveguides for the purpose of communication in an integrated circuit on a silicon substrate has also been demonstrated. The next step is to incorporate erbium into the glass waveguides in order to produce optical amplifiers and lasers on the silicon substrate. Polman *et al.* [79,80] studied the photoluminescence (PL) of erbium implanted into silica films and into phosphosilicate glass (P glass). Si₃N₄ as a host was also studied but this work will not be discussed. The energies used were near 3 MeV and fluences were $3.8\text{--}5 \times 10^{15}$ ions/cm². The implantation of silica allowed measurable PL (at 1.54 μm) intensity at room temperature without annealing (unlike erbium-implanted semiconductors). By annealing in the 700-900 °C range the lifetime of the fluorescence decay increased from the as-implanted value of 6 ms to about 15 ms; this increase comes about by annealing of the radiation-induced damage. In the case of P-glasses, no annealing was required as the lifetime (12 ms) and the PL intensity remain fairly constant upon annealing over the temperature range of 300-1000 °C. The authors

speculated that this softer glass more easily accommodates the damage and the phosphorous forms a cage around the implanted erbium.

In another paper [81] the authors studied the stability of erbium-implanted silica films using the radiation damage created by a subsequent implants of MeV carbon, silicon and germanium. They found that the lifetime was affected by fluences as low as 10^{11} ions/cm² and saturation of the induced changes occurs at a fluences higher than 10^{14} ions/cm². For a sample annealed at 900 °C the lifetime changes from 14 ms to about 7 ms. These effects were attributed to the electronic energy deposition of the ions used in the second implant.

Very recently Snoeks *et al.* [82] implanted a soda-lime silicate glass with 500 keV erbium ions. Erbium concentrations in the range 0.09-1.9 at.% were obtained. The characteristic photoluminescence of Er³⁺ was observed at room temperature in as-implanted glass. The photoluminescence intensity increased by an order of magnitude after annealing above 500 °C, as a result of annihilation of implantation induced defects. The photoluminescence efficiency decreases for increasing erbium concentration due to concentration quenching caused by Er-Er interactions.

Adler *et al.* [83] used the extended X-ray absorption fine structure (EXAFS) technique to study the coordination of erbium ions implanted in Czochralski-grown silicon (CZ-Si) samples, which exhibit strong luminescence at 1.54 μm. They have found that erbium presents a local sixfold coordination of oxygen atoms. On the contrary erbium implanted into high-purity float-zones silicon (FZ-Si) samples, which are optically inactive, is coordinated to 12 silicon atoms. The authors concluded that the optically active specie of erbium, in CZ-Si, involves sixfold bonding of erbium to oxygen impurity atoms, resembling Er₂O₃, with a minor role of the silicon host. In FZ-Si, which contain much less oxygen impurities, erbium

is optically inactive and the coordination to silicon resembles that of ErSi_2 . Such conclusions are consistent with EXAFS results for optically active erbium introduced into silica-based optical fibers by the melting process [84].

6. Conclusions

Implantations of reactive species in silica glasses causes the formation of compounds due to chemical interactions. Such phenomenon can be explained using a two-step model where the ballistic effects are separated from the chemical (thermodynamic) driving forces [85]. However, the introduction of thermodynamic consideration is limited by uncertainties on the correct values for the local temperature and on the assumption of the implanted ion interaction with substrate separate atomic species or groups. Both of these fact influence the Gibbs' free energy values to be used in calculations.

Nanometer size metal clusters may be synthesized by ion implantation. The presence and size of such clusters depend on the type of substrate and, for the same substrate, to the implanted species and implantation parameters. Such results imply that the aggregation behaviour is not controlled by the local temperature during implantation.

The silica-metal composites exhibit a Kerr-type non-linear susceptibility. The measured non-linear refractive-indexes compare well to II-VI semiconductor nanocrystallites and are much larger than that of colloidal melt glasses. Ion implantation may produce metal nanoclusters in a variety of insulators in geometries useful for optoelectronic devices. A larger investigation is necessary, in particular, for a correct evaluation of

third order non-linear susceptibility avoiding the thermal contribution effects.

Acknowledgements

This work has been partially supported by Italian M.U.R.S.T. and C.N.R. (within the project "Materiali Speciali per Tecnologie Avanzate"). The work of G.W. Arnold was supported by the U.S. Department of Energy under contract number DE-AC04-76DP00789.

94AL85000

References

- [1] R.A. Weeks, in: Glasses and Amorphous Materials, ed. J. Zarzycki (VCH, Weinheim, 1991) p. 331 and references therein.
- [2] G.W. Arnold, in Homage to Galileo (Collection of Invited Papers of the international conference From Galileo's "Occhialino" to Optoelectronics: Frontiers of Optical Systems and Materials, Padova, Italy, 1992), ed. P. Mazzoldi (CLEUP, Padova, 1992) p. 3 and references therein.
- [3] P.D. Townsend, in Modifications Induced by Irradiation of Glasses, ed. P. Mazzoldi (Elsevier, Amsterdam, 1992) p. 73 and references therein.
- [4] A.P. Webb and P.D. Townsend, J. Phys. D 8 (1975) 1567.
- [5] C. Wang, Y. Tao and S. Wang, J. Non-Cryst. Solids 52 (1982) 589.
- [6] I.K. Naik, Appl. Phys. Lett. 43 (1983) 519.
- [7] I.K. Naik, in Processing of Guided Wave Optoelectronic Materials, ed. R.L. Holman and D.M. Smyth, Proc. SPIE 460 (1984) 56.
- [8] A. Carnera, P. Mazzoldi, A. Boscolo-Boscoletto, F. Caccavale, R. Bertoncello, G. Granozzi, I. Spagnol and G. Battaglin, J. Non-Cryst. Solids 125 (1990) 293.
- [9] T. Tagami, K. Oyoshi and S. Tanaka, Mat. Res. Soc. Symp. Proc. Vol. 128 (1989) 519 and Mat. Res. Soc. Symp. Proc. Vol. 157 (1990) 149.
- [10] G.W. Arnold, R.K. Brow and D.R. Myers, J. Non-Cryst. Solids 120 (1990) 234.
- [11] K. Oyoshi, T. Tagami and S. Tanaka, J. Appl. Phys. 68 (1990) 3653.
- [12] H. Hosono, Y. Abe, K. Oyoshi and S. Tanaka, Phys. Rev. B43 (1991) 1193.
- [13] P. Mazzoldi, A. Carnera, F. Caccavale, M.L. Favaro, A. Boscolo-Boscoletto, G. Granozzi, R. Bertoncello and G. Battaglin, J. Appl. Phys. 70 (1991) 3528.

- [14] H. Hosono, Nucl. Instr. and Meth. B65 (1992) 375.
- [15] G. Battaglin, A. Boscolo-Boscoletto, F. Caccavale, G. De Marchi, P. Mazzoldi and G.W. Arnold, in Modifications Induced by Irradiation of Glasses, ed. P. Mazzoldi (Elsevier, Amsterdam, 1992) p. 91.
- [16] P. Mazzoldi, F. Caccavale, E. Cattaruzza, A. Boscolo-Boscoletto, R. Bertoncello, A. Glisenti, G. Battaglin and C. Gerardi, Nucl. Instr. and Meth. B65 (1992) 367.
- [17] G. Battaglin, in Modifications Induced by Irradiation of Glasses, ed. P. Mazzoldi (Elsevier, Amsterdam, 1992) p. 11 and references therein.
- [18] R. Bertoncello, A. Glisenti, G. Granozzi, G. Battaglin, E. Cattaruzza and P. Mazzoldi, Mat. Res. Soc. Symp. Proc. Vol. 268 (1992) 325.
- [19] R. Bertoncello, A. Glisenti, G. Granozzi, G. Battaglin, E. Cattaruzza and P. Mazzoldi, J. Non-Cryst. Solids 162 (1993) 205.
- [20] L. Genzel, T. P. Martin, U. Kreibig, Z. Physik B2 (1975) 339.
- [21] K. Koizumi, Proc. XVI International Congress on Glass, vol. 1, ed. A. Durán and J.M. Fernández Navarro (S.E. de Cerámica y Vidrio, Madrid, 1992) p. 45.
- [22] J. E. Goell, R. D. Standley, Proc. IEEE Vol. 58 (1970) 1504.
- [23] E.M. Vogel, J. Am. Ceram. Soc. 72 (1989) 719.
- [24] G.I. Stegeman and C.T. Seaton, J. Appl. Phys. 58 (1985) 57.
- [25] Y. Fainman, J. Ma and S. H. Lee, Material Science Report 9 (1993) 53.
- [26] O. Knacke, O. Kubaschewski and K. Hesselmann ed., Thermochemical Properties of Inorganic Substances, Second Edition (Springer-Verlag, Berlin, 1991).
- [27] G.W. Arnold, G. Battaglin, A. Boscolo-Boscoletto, F. Caccavale, G. De Marchi, P. Mazzoldi and A. Miotello, Nucl. Instr. and Meth. B65 (1992) 387.

- [28] G.W. Arnold, G. Battaglin, A. Boscolo-Boscoletto, F. Caccavale, G. De Marchi and P. Mazzoldi, *Mat. Res. Soc. Symp. Proc.* Vol. 235 (1992) 407.
- [29] G. Fuxi, *Optical and Spectroscopic Properties of Glass* (Springer-Verlag, New York, 1992).
- [30] R.H. Magruder III, Li Yang, R.F. Haglund, Jr., C.W. White, Lina Yang, R. Dorsinville and R.R. Alfano, *Appl. Phys. Lett.* 62 (1993) 1730.
- [31] K. Fukumi, A. Chayahara, K. Kadono, T. Sakaguchi, Y. Horino, M. Miya, J. Hayakawa and M. Satou, *Jpn. J. Appl. Phys.* 30, 4B (1991) 742.
- [32] F. Hache, D. Ricard, C. Flytzanis and U. Kreibig, *Appl. Phys. A* 47 (1988) 347.
- [33] J. W. Haus, N. Kalyaniwalla, R. Inguva, M. Bloemer and C. M. Bowden, *J. Opt. Soc. Am. B* 6 (1989) 797.
- [34] K. Becker, L. Yang, R.F. Haglund, Jr., R.H. Magruder III, R.A. Weeks, and R.A. Zuhr, *Nucl. Instr. Meth.* B59/60 (1991) 1304.
- [35] R.F. Haglund, Jr., R.H. Magruder III, S.H. Morgan, D.O. Henderson, R.A. Weller, L. Yang and R.A. Zuhr, *Nucl. Instr. Meth.* B65 (1992) 405.
- [36] R.F. Haglund, Jr., L. Yang, R.H. Magruder III, J.E. Witting, K. Becker and R.A. Zuhr, *Optics Letters* 18 (1993) 373.
- [37] P. N. Butcher and D. Cotter, *The Elements of Non-linear Optics* (Cambridge University Press, Cambridge, UK. 1990).
- [38] W.P. Halperin, *Rev. Mod. Phys.* 58 (1986) 533.
- [39] F. Hache, D. Ricard and C. Flytzanis, *J. Opt. Soc. Am. B* 3 (1986) 1647.
- [40] Y. R. Shen, *The Principles of Non-linear Optics* (John Wiley & Sons, New York, 1984).
- [41] M. Sheik-Bahae, A. A. Said, T. Wei, D. J. Hagan and E. W. Van Stryland, *IEEE J. Quantum Electron.* 26 (1990) 760.
- [42] G. I. Stegeman and R. H. Stolen, *J. Opt. Soc. Am. B* 6 (1989) 652.

- [43] R.H. Magruder III, R.A. Zuhr and R.A. Weeks, Nucl. Instr. Meth. B 59/60 (1991) 1308.
- [44] R.H. Magruder III, R.A. Weeks, R.A. Zhur and G. Whichard, Nucl. Instr. Meth. 129 (1991) 46.
- [45] H. Hosono, Y. Abe, N. Matsunami, Appl. Phys. Lett. 60 (1992) 2613.
- [46] H. Hosono, Y. Ikuhara, Y. Abe, R.A. Weeks, J. Mat. Sci. Lett. 11 (1992) 1257.
- [47] H. Hosono, H. Fukushima, Y. Abe, R.A. Weeks and R.A. Zuhr, J. Non-Cryst. Solids 143 (1992) 157.
- [48] D.M. Trotter, J.W. Schreurs and P. A. Tick, J. Appl. Phys. 53 (1982) 4657.
- [49] R. Rubbin, J. Appl. Phys. 59 (1986) 1355.
- [50] P.W. Baumeister, Phys. Rev. 121 (1961) 359.
- [51] D.C. Reynolds and T.C. Collins, "Excitons" (Academic Press, New York, 1981).
- [52] G.W. Arnold and J.A. Borders, J. Appl. Phys. 48 (1977) 1488.
- [53] P. Mazzoldi, L. Tramontin, A. Boscolo Boscoletto, G. Battaglin and G.W. Arnold, Nucl. Instr. and Meth. B80/81 (1993) 1192.
- [54] R.A. Weeks, H. Hosono, A. Zuhr, R.H. Magruder III and H. Mogul, Mat. Res. Soc. Symp. Proc. Vol. 152 (1989) 115.
- [55] G.W. Arnold, P. Mazzoldi, L. Tramontin, A. Boscolo-Boscoletto and G. Battaglin, Mat. Res. Soc. Symp. Proc. Vol. 279 (1993) in press.
- [56] P. Mazzoldi, F. Caccavale, E. Cattaruzza, L. Tramontin, A. Boscolo-Boscoletto, R. Bertoncello, F. Trivillin, G.W. Arnold, and G. Battaglin, this conference.
- [57] P. Mazzoldi, F. Caccavale, G. Battaglin, A. Boscolo Boscoletto, F. Priolo and G.W. Arnold, paper presented at the IUMRS-ICAM-93 conference, Tokyo, Aug. 31-Sept. 4, 1993.

- [58] F. Caccavale, P. Mazzoldi, L. Tramontin, G. Battaglin and A. Boscolo-Boscoletto, Proc. XVI International Congress on Glass, vol. 4, ed. A. Durán and J.M. Fernández Navarro (S.E. de Cerámica y Vidrio, Madrid, 1992) p. 205.
- [59] G. Mie, Ann. Physik 25 (1908) 377.
- [60] D. Briggs and M.P. Seah, in Practical Surface Analysis -Vol 1, second edition, ed. D. Briggs and M.P. Seah (Wiley , Chichester, 1990).
- [61] G.W. Arnold and F.L. Vook, Rad. Effects 14 (1972) 157.
- [62] D. Ricard, P. Roussignol and C. Flytzanis, Opt. Lett. 10 (1985) 511.
- [63] R.H. Magruder III, D.O. Henderson, S.H. Morgan and A. Zhur, J. Non-Cryst. Solids 152 (1993) 258.
- [64] D.O. Henderson, R.H. Magruder III, S.H. Morgan and A. Zhur, in "Properties and Characteristics of Optical Glass III", Proc. SPIE in press.
- [65] D.W. Hall, M.A. Newhouse, N.V. Borrelli, W.H. Dumbhaugh and D.L. Weidman, Appl. Phys. Lett. 54 (1989) 1293.
- [66] M.E. Lines, J. Appl. Phys. 69 (1991) 258.
- [67] S. Parke and R.S. Webb, Phys. Chem. Solids 34 (1973) 85.
- [68] J.S. Stroud and J. Lell, J. Am. Ceram. Soc. 54 (1971) 554.
- [69] A. Paul, Phys. Chem. Glasses 11 (1970) 46.
- [70] W.T. Doyle, Phys. Rev. 11 (1958) 1067.
- [71] A. Perez, M. Treilleux, T. Capra and D.L. Griscom, J. Mater. Res. 2 (1987) 910.
- [72] G.W. Arnold, J. Appl. Phys. 46 (1975) 4466.
- [73] P. Roussignol, D. Ricard, K.C. Rustagi and C. Flytzanis. Opt. Commun. 55 (1985) 143.
- [74] H. Hosono, Y.Y. Suzuki, Y. Abe, Y.L. Lee, K. Oyoshi and S. Tanaka, J. Non-Cryst. Solids 142 (1992) 287.

- [75] H. Hosono, Y. Abe, Y.L. Lee, T. Tokizaki and A. Nakamura, Appl. Phys. Lett. 61 (1992) 2747.
- [76] K. Oyoshi, T. Tagami, K. Yamashita and S. Tanaka, Nucl. Instr. and Meth. B59/60 (1991) 1324.
- [77] Y. Takeda, T. Hioki, T. Motohiro and S. Noda, this conference.
- [78] G.L. Zhang, W.H. Liu, F. Xu and W.H. Hu, Appl. Phys. Lett. 61 (1992) 2527.
- [79] A. Polman, D.C. Jacobson, D.J. Eaglesham, R.C. Kistler and J.M. Poate, J. Appl. Phys. 70 (1991) 3778.
- [80] A. Polman, D.C. Jacobson, A. Lidgard, J.M. Poate and G.W. Arnold, Nucl. Instr. and Meth. B59/60 (1991) 1313.
- [81] A. Polman and J.M. Poate, J. Appl. Phys. 73 (1993) 1669.
- [82] E. Snoeks, G.N. van den Hoven and A. Polman, J. Appl. Phys. 73 (1993) 8179.
- [83] D.L. Adler, D.C. Jacobson, D.J. Eaglesham, M.A. Marcus, J.L. Benton, J.M. Poate and P.H. Citrin, Appl. Phys. Lett. 61 (1992) 2181.
- [84] M.A. Marcus and A. Polman, J. Non-Cryst. Solids 136 (1992) 260.
- [85] R. Kelly, Mat. Sci. Eng. A115 (1989) 11.

Figure captions

Figure 1: Si(2p_{3/2+1/2}) doublet, at different depths from the surface, for a 30 keV titanium implanted silica sample [19].

Figure 2: Ti(2p) peak, at a depth close to R_p for a 30 keV titanium implanted silica sample [19].

Figure 3: W(4f) XPS peak, at a depth close to R_p , for a 200 keV, 5×10^{16} ions/cm², tungsten-implanted sample [19].

Figure 4: SIMS depth profiles of the implanted elements after the implantation with 2×10^{17} ions/cm², 100 keV nitrogen ions in (a) silica and silica implanted with silicon, (b) silica implanted with titanium and (c) silica implanted with tungsten [19].

Figure 5: Degenerate four-wave mixing configurations.

Figure 6: Z-scan configuration. The sample is moved along the z direction. The self-focussing effect increases the beam divergence for negative values of z, and decreases the divergence for positive values. A typical Z-scan output is also shown.

Figure 7: Two all-optical switching devices scheme, together with the response in the case of linear (dashed lines) and non-linear (solid lines) materials.

Figure 8: 160 keV, 5×10^{16} ions/cm² Cu-implanted silica: Cu concentration from RBS and particle diameters from TEM as a function of depth. R_p and ΔR_p indicate mean projected range and range straggling calculated using the TRIM code [47].

Figure 9: Values of $\chi^{(3)}$ (in esu), measured for a 160 keV, 10^{17} ions/cm², copper-implanted-silica, superimposed on the linear absorbance spectrum (right-hand axis) [36].

Figure 10: RBS spectra for 270 keV, 1.5×10^{16} ions/cm², silver-implanted silica (CFS), Pyrex (PYR) and soda-lime (SLG) glasses. Only the energy region corresponding to scattering from silver and the heavier constituents of the glasses has been reported [53].

Figure 11: RBS spectra for 270 keV, 1.5×10^{16} Ag/cm² and 100 keV, 1.5×10^{17} N/cm², nitrogen-irradiated silver-implanted silica (CFS), Pyrex (PYR) and soda-lime (SLG) glasses. Only the energy region corresponding to scattering from silver and the heavier constituents of the glasses has been reported [53].

Figure 12: Histogram of the colloid radii obtained from TEM analysis of the silver-implanted CFS sample.

Figure 13: Extinction coefficient per ion for gold implanted silica: as-implanted, annealed in O₂ at 900 °C and annealed in a mixture of argon with 4% H₂ at 1100 °C [30].

Fig 1

Fig 3

Fig. 4

Fig 6

directional coupler (self-induced switching)

Mach-Zehnder interferometer

Fig 8

Fig. 9

01 Exp

Fig 11

Fig. 12

Fig. 13

**DATE
FILMED**

1/31/94

END