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Nuclear Instruments and Methods in Physics Research B 236 (2005) 73–80

NIM B
Beam Interactions with Materials & Atoms

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# Precipitation of C, Si and metals nanoparticles in silicon-based gels induced by swift heavy ion irradiation

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Available online 24 May 2005

**Abstract**

Studies of irradiation effects in inorganic polymers and gels performed at CSNSM during the last ten years are summarized, and new results concerning the effect of the density of transferred energy on the precipitation kinetics of C, Si and metal clusters are presented. The precipitation yield as a function of the fluence of ions with different masses and energies was investigated by means of various spectroscopies, depending on the particles nature. The rates of gel to ceramics conversion and of C, Si and metal precipitation are determined by the density of electronic excitations and nuclear collisions have little effect. Particles formed by ion irradiation show a narrower size distribution and, consequently, more interesting characteristics for magnetic or optical applications than those formed in heat treated gels.


*PACS:* 61.82.−Bg; 78.67.−Bf; 81.20.Fw

*Keywords:* Sol-gel; Nanomaterial; Ion irradiation

## 1. Introduction

Materials with nanometric structures are interesting in many respects because of the the change in the properties of solid phases in this regime of transition between the bulk and molecular scales. Sol–gel chemistry is a very convenient technique for producing nanomaterials with a wide range of compositions. The rate of reactions occurring during the gels thermal processing and the evolution of some components are however not well controlled. The obtained ceramics are often porous, heavily

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0168-583X/$ - see front matter 
doi:10.1016/j.nimb.2005.03.256

cracked, and the particles of secondary nanophase tend to exhibit a wide range of sizes.

Studies of irradiation effects in inorganic polymers and gels performed during the last ten years [1–3] demonstrated the interest of using this ion beam route instead of thermal processing for releasing only H and obtaining dense ceramic films, free of cracks (the cracks in heat treated films are principally due to the mismatch of the expansion coefficients of film and substrate) [1]. The out-of-equilibrium nature of the ion irradiation chemistry permits also to promote selectively some reactions between the gel components, among other reasons because the formed radicals are able to migrate only at short range.

This paper reports the effects of the linear densities of electronic and nuclear energy transfer (LET) on the precipitation of C, Si and metals in silicon-based gels. Different physical quantities are used for assessing the precipitation kinetics as a function of the fluence, mass and velocity of ions, depending on the particles nature. Properties of particles formed under ion irradiation are compared to those of particles obtained by heat treatment of the same precursors.

## 2. Experiments

The studied gels were prepared from ethoxides with following formulae: $Si(OC_2H_5)_4$, $Si(CH_3)(OC_2H_5)_3$, $Si(C_6H_5)(OC_2H_5)_3$, and $Si(H)(OC_2H_5)_3$, labeled respectively TEOS, MTES, PTES and TH. TEOS, MTES, PTES and mixtures of these precursors (for obtaining films of better optical qualities than with pure PTES) were hydrolyzed as usual by addition of 2 mol of water and $10^{-2}$ mol of nitric acid for 1 mol of ethoxide in ethanolic solution, with stirring for 1 h at room temperature, then films with a thickness of 400–500 nm were deposited by spinning the filtered gel on Si wafers. Triethoxysilane (TH) mixed in equimolar proportion with pure ethanol was simply stirred during 5 min before adding salts of various metals M (M = Fe, Co, Ni, Cu). The TH:M filtered gels were used immediately for spinning films in order to hamper the progressive hydrolysis of Si–H bonds. Analyses of TH films by means of the $^{12}C(d,p)^{13}C$ nuclear reaction show that this simple procedure provides gels containing less than 2 at.% C. The composition of pristine, irradiated or annealed films was determined accurately by combining RBS, NRA and ERDA analyses. The atomic compositions of pristine films are $Si_1O_2C_{0.05}H_{1.5}$ (TEOS), $Si_1O_{1.9}C_{1.0}H_{3.9}$ (MTES), $Si_1O_{1.7}C_{6.0}H_{6.4}$ (PTES) and $Si_1O_{1.25}C_{0.05}H_{1.0}$ (TH). These atomic ratios indicate that chains of MTES and PTES are much less branched and cross-linked than those of TEOS and TH. The O/Si content in TH films increases up to 1.4–1.5 after irradiation or annealing when no salt is added to the precursor, and up to 1.7 in films from sols containing 10–20 mol.% $MNO_3{\cdot}xH_2O$ (M = Fe, Ni, Co) or 20% $CuCl_2{\cdot}2H_2O$ ($CuNO_3$ was not used because this salt catalyses the precipitation of silica).

Ions of various masses and energies in the MeV range were used for varying the yields of electronic excitations and atomic displacements in the films. The electronic and nuclear stopping powers, $S_e$ and $S_n$, of 3 MeV Au ions are of same order of magnitude (1.5 and 3.0 keV/nm respectively), and the total electronic LET obtained by adding the energy lost by recoil atoms and primary ions is equal to $S_n$. This value of 3 keV/nm will be used as $S_e$ of 3 MeV Au ions in the following. A few experiments were performed on MTES and PTES films with 900 keV Xe ions having a similar $S_e/S_n$ ratio ($S_e = 0.7$ keV, $S_n = 1.7$ keV). Si ions with an energy of 3 MeV were selected for producing a comparable linear density of electronic excitations ($S_e = 1.8$ keV/nm) and much less atomic displacements ($S_n = 100$ eV/nm). 1 MeV He ions also lose their energy essentially in electronic excitations with a lower LET of 300 eV/nm. 100 MeV Ag and Au ions were used for increasing the $S_e$ value up to 15–20 keV/nm while keeping $S_n$ at a low level of 300 eV/nm. Note finally that all these ions stop at some micrometers in the substrate. The experimental conditions of structural characterizations performed after irradiation or annealing, by means of X-ray diffraction at grazing incidence, TEM with energy filtering of inelastically scattered electrons (EFTEM), Raman scattering and FTIR, electron spin resonance (ESR) and optical techniques, are detailed in other papers [1,4,5].