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ARTICLE *in* APPLIED PHYSICS LETTERS · FEBRUARY 2003

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# Chemical composition and local structure of plasma enhanced chemical vapor-deposited Si nanodots and their embedding silica matrix

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(Received 10 July 2002; accepted 13 December 2002)

X-ray absorption measurements in total electron yield mode have been carried out on Si nanodots embedded in amorphous silica produced by plasma enhanced chemical vapor deposition (PECVD). The amount of Si atoms composing the Si nanodots and the chemical composition of the amorphous host matrix has been determined thanks to the comparison with Rutherford backscattering spectrometry data. The influence of nitrogen, incorporated during the PECVD procedure, on the structure of the host silica matrix has been discussed. © 2003 American Institute of Physics.  
[DOI: 10.1063/1.1543641]

In the last two years, many reports on Si nanodots (Si-nd) embedded in amorphous silica matrix have been published, following on the experimental findings about their optical gain.<sup>1</sup> The various techniques and experimental conditions used to prepare such systems, give rise to samples with different chemical, structural, and optical properties.<sup>2,3</sup> As a consequence, the interpretation of the light emission mechanism given by different authors is often controversial also due to the lack of accurate sample characterization. Important information concerns the amount of Si atoms segregated in the Si-nd, the evaluation of size and distribution of the clusters, and the chemical composition and structure of the host matrix, which can be influenced by the presence of contaminants, local defects, or inhomogeneities.

In this letter, we present the results of studies performed on a set of Si-nd samples produced by plasma enhanced chemical vapor deposition (PECVD) and thermally annealed at 1250 °C, characterized by different nanodots mean sizes and luminescence bands. We show that original information on the amount of Si atoms composing the Si-nd and the chemical composition of the amorphous host matrix can be obtained by combining Rutherford backscattering spectrometry (RBS) and x-ray absorption spectroscopy (XAS).

In PECVD-grown samples, N atoms may be incorporated in the matrix as impurities due to the use in the preparation procedure of N<sub>2</sub>O as one of the gaseous precursors. The presence of N atoms in the amorphous SiO<sub>2</sub> network introduces defect states localized at Si-N bonds. These are active in hole trapping and transport, and strongly influence

the balance between radiative and nonradiative decay processes.<sup>4–6</sup> Moreover, the formation of Si oxynitrides in the silica matrix plays a fundamental role in enhancing the dielectric constant and the refractive index, in lowering the optical band gap and in reducing structural strains<sup>7</sup> with respect to SiO<sub>2</sub>. In spite of the huge research activity devoted to reveal the role of N in silicon oxynitrides,<sup>4,5,8–10</sup> a clear compositional and structural picture is still lacking.

Among the various techniques employed for structural characterization, XAS has contributed to investigate nanocrystalline and amorphous materials.<sup>11–13</sup> In this work, the analysis of XAS spectra at the Si *K* edge, collected in total electron yield (TEY) mode, has allowed an independent assessment of the amount of Si atoms clustered in Si-nd. Moreover, from the comparison with RBS data, it has been possible to give a quantitative compositional description of the amorphous matrix including the role of N atoms. A compositional model interpreting the experimental results is presented and discussed.

Silicon nanodots have been produced by PECVD of substoichiometric silicon oxide (SiO<sub>x</sub>) followed by high-temperature annealing.<sup>3</sup> In this way, the deposited homogeneous SiO<sub>x</sub> layer is changed to a biphasic material, in which Si nanodots are dispersed in an amorphous matrix.<sup>14</sup> SiO<sub>x</sub> stoichiometric samples ( $x=2$ ) contain 33% of Si atoms, while substoichiometric samples ( $x<2$ ) have an excess of Si atoms available for the formation of Si-nd. By varying the stoichiometry of the film, a change of the mean size of Si-nd formed after thermal annealing is obtained.<sup>3</sup>

We present here the results relative to a set of samples with different Si content (35, 37, 39, 42, and 46 at. %), annealed for 1 h at 1250 °C in ultrapure N<sub>2</sub> atmosphere. In agreement with quantum confinement theory, the photolumi-

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TABLE I. Chemical composition (expressed as atomic percent) of a set of PECVD Si-nd obtained by increasing the Si content of  $\text{SiO}_x$  films annealed at 1250 °C. The accuracy is  $\pm 1\%$  for RBS measurements and  $\pm 0.5\%$  for TEY best fit.

Si total content (from RBS) (%)	O total content (from RBS) (%)	N total content (from RBS) (%)	Si in Si-nd (measured by TEY) (%)	excess Si atoms in the matrix (%)
35	51	14	2.5	7
37	51	12	5.5	6
39	49	12	9	5.5
42	48	10	10.5	7.5
46	46	8	13.5	9.5

nescence (PL) spectra of these samples show a redshift (from 760 to 930 nm) with increasing the Si content, because of the increasing mean size of the Si-nd (from less than 1 to 2.1 nm in radius) as documented by the comparison between PL and transmission electron microscopy data.<sup>3,15</sup>

Composition and thickness of the annealed samples were determined by RBS measurements, carried out by using a 1.6 MeV  $\text{He}^+$  beam in random configuration. Samples were about 200 nm thick and homogeneous in depth. As shown in Table I (columns 1–3), RBS measurements give the elemental composition of the samples, without distinguishing between Si atoms in the nanodots and in the amorphous matrix. Furthermore, RBS data indicate variable and significant content of N atoms.<sup>3</sup> This evidence requires a more complete quantitative compositional description, including information on the chemical bonds. To this purpose, RBS data have been coupled to XAS data. X-ray absorption measurements were carried out at Super-ACO (LURE–Orsay, F) on the SA32 x-ray beamline. The absorption spectra were recorded at the Si  $K$  edge in the range 1830–1870 eV by detecting the total yield of electrons escaping from the sample. The sampling depth of the TEY-XAS technique at Si  $K$  edge energy is about 100 nm for both  $c$ -Si and  $\text{SiO}_2$ ,<sup>16</sup> i.e., comparable to the thickness of samples but not too long to detect the contribution of the Si substrate.

TEY spectra show two main features (Fig. 1, continuous line): the initial part of the absorption spectrum of Si nanodots, beginning at 1839 eV, and the absorption spectrum of silica, characterized by a sharp peak (white line), at about 1847 eV, followed by the first extended x-ray absorption fine structure (EXAFS) oscillation. The intensity of the absorption coefficient of Si in Si-nd increases with the Si content of the samples, confirming that excess Si atoms form Si-nd. To quantitatively assess the amount of Si atoms in the nanodots, we have reproduced the experimental TEY spectra by a linear combination of  $c$ -Si and  $a$ - $\text{SiO}_2$  reference absorption spectra, reported in Fig. 2. As shown in Fig. 1 for all samples the best fit (dashed line) well reproduces the absorption coefficient; only the main absorption peak of silica at about 1847 eV is systematically underestimated. However, it is known that the white line of silica is very sensitive to small changes in the local environment; in fact, strain effects or small chemical bond modifications induce changes in the electronic density and hence in the white-line intensity.<sup>17,18</sup>

The amount of Si–Si bonds, as obtained by the fitting procedure of the TEY spectra, is shown in column 4 of Table

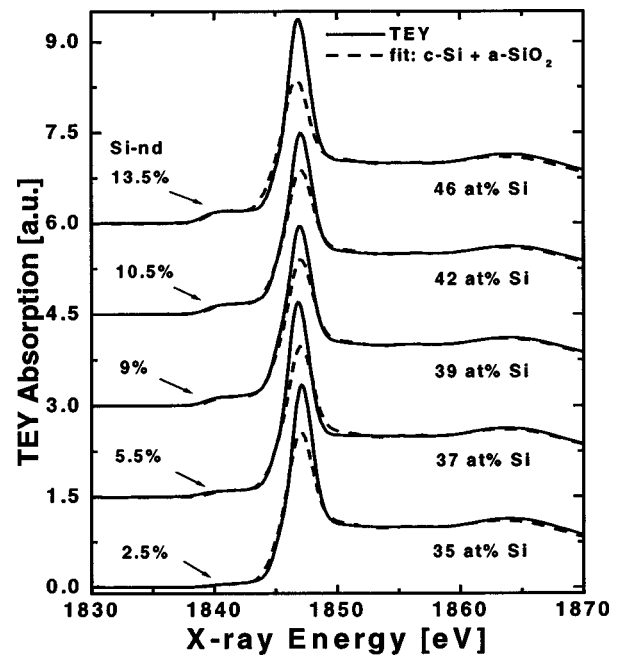


FIG. 1. TEY absorption spectra (continuous lines) at the Si  $K$  edge of a set of PECVD samples obtained with increasing the Si content and annealed at 1250 °C. Simulated spectra (dashed lines) obtained by a combination of the  $c$ -Si and  $a$ - $\text{SiO}_2$  reference spectra shown in Fig. 2.

I (best-fit accuracy:  $\pm 0.5\%$ ). For each sample, the sum of this value and of the amount of Si atoms bonded to oxygen (evaluated from RBS data within the hypothesis of an O/Si ratio of 2, as in stoichiometric silica) is less than the Si total content obtained from RBS measurements (column 1). The difference (column 5) accounts for Si atoms that are neither bonded to O nor enclosed in Si-nd. Therefore, from the comparison between TEY and RBS data, we conclude that our systems cannot be simply described in terms of Si-nd and silica network; we suggest that the excess Si atoms in the amorphous matrix are coordinated to N atoms. Thus, from a compositional point of view, the samples are constituted of Si atoms clustered in Si-nd, Si atoms tetrahedrally bonded to O as in  $\text{SiO}_2$  and Si atoms coordinated to N.

It is worth noting that for the samples with low Si content (35, 37, and 39 at. % of Si) the ratio between the excess of Si (column 5 of Table I) and the amount of N (column 3) is the same as in  $\text{SiO}_2$ , i.e., 1/2. The simplest interpretation

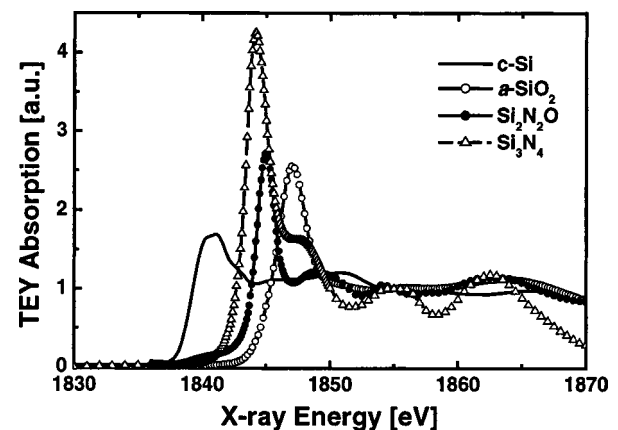


FIG. 2. TEY absorption spectra at the Si  $K$  edge of  $c$ -Si,  $a$ - $\text{SiO}_2$ ,  $\text{Si}_3\text{N}_4$ , and  $\text{Si}_2\text{N}_2\text{O}$  reference samples, normalized at about 1855 eV.

for the structure of these samples is to consider N atoms as substitutional of O in the formation of tetrahedra  $\text{SiX}_4$  (with  $\text{X}=\text{O}, \text{N}$ ), participating to the formation of a Si oxynitride network  $\text{SiN}_x\text{O}_{2-x}$ , very similar to the  $\text{SiO}_2$  structure. When N atoms are substitutional of oxygen atoms in the silica-like network, we expect that the XAS spectrum is very similar to that of amorphous  $\text{SiO}_2$  [as observed in TEY–XANES (x-ray absorption near edge structures) spectra] and differences could be appreciable only in the long-range order structure, which can be probed only by EXAFS measurements.

At higher Si content, the Si/N ratio becomes 3/4 for the sample with 42 at. % of Si and greater than 1 for the sample with 46 at. % of Si. The structure of the samples with higher Si content could be related to the formation of silicon nitride ( $\text{Si}_3\text{N}_4$ ) or oxynitride ( $\text{Si}_2\text{N}_2\text{O}$ ) phases well separated from the silica network. However, the XANES spectra in Fig. 1 do not show significant modifications in the region where Si–N bonds are expected to contribute and no experimental evidence of  $\text{Si}_3\text{N}_4$  or  $\text{Si}_2\text{N}_2\text{O}$  is detectable, as it can be deduced by comparing the spectra in Fig. 1 with those of the reference samples shown in Fig. 2.<sup>19</sup> Thus, we suggest for the amorphous matrix an average composition of the type  $\text{SiN}_x\text{O}_y$ , where the N atoms assume different oxidation states (from  $-2$  to  $-4$ ) by increasing the Si excess.

An alternative interpretation of the data is possible: if in all samples N atoms have the same oxidation state and local coordination (i.e., N atoms are substitutional of oxygen atoms in the silica-like network), we can conclude that the matrix is still substoichiometric with an excess of Si atoms randomly distributed and not segregated in Si–nd. As a matter of fact, the N and O atoms are not enough to bond, in a 2:1 ratio, all the Si atoms that are not enclosed in Si–nd, as expected from TEY results. A possible reason for this is that, for high Si content, the annealing temperature of  $1250^\circ\text{C}$  is still too low to allow a complete clustering of the Si phase. Changes of the PL properties observed in these systems,<sup>3</sup> in the annealing temperature range  $1250$ – $1300^\circ\text{C}$ , are in agreement with this hypothesis. A detailed XAS study of the local structure around Si as a function of the annealing temperature is currently in progress.

The present results have been compared with refractive index measurements:<sup>20</sup> they show that a simple model where Si–nd are embedded in a  $\text{SiO}_2$  matrix is not able to reproduce the experimental values; better agreement has been found by using a more refined model, where Si–nd are embedded in a medium composed of both  $\text{SiO}_2$  and  $\text{Si}_3\text{N}_4$ . Despite the assumption of a complete phase separation is a rather crude approximation and does not match TEY results, the good agreement between estimate and experimental results found in Ref. 20 supports the present findings about the N chemistry. Moreover, we note that the presence of N atoms does not degrade the optical quality of the samples. Indeed,

PL measurements show high intensity signals, demonstrating that no large defect density, which would prevent radiative recombination, is present.

In conclusion, in this letter we have reported a detailed characterization of PECVD samples containing Si nanodots embedded in an amorphous matrix. The amount of Si atoms clustered in Si–nd has been assessed. Moreover it has been shown that the matrix cannot be simply described as  $\text{SiO}_2$ , but significant incorporation of N atoms occurs. The actual structure of the amorphous  $\text{SiN}_x\text{O}_y$  matrix is dependent on Si concentration, deposition parameters, and annealing treatments.

This work was supported by INFM (RAMSES advanced project and Large Facilities grants) and by TMR Program of the European Community for measurements at LURE Laboratories (Orsay-France).

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