

Combinatorial ion synthesis and ion beam analyses of materials libraries on thermally grown SiO₂

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Abstract

We first report a method combining ion implantation and physical masking to generate material libraries of various ion-implanted samples. This approach offers rapid synthesis of samples with potential new compounds formed in the matrix, which may have specific luminescent properties. The depth-resolved cathodoluminescence (CL) measurements, accompanied with Rutherford backscattering spectrometry (RBS) and proton elastic scattering (PES) revealed some specific optical properties in the samples correlated with implanted ion distributions. These measurements are capable of nondestructively and rapidly characterizing the composition and the inhomogeneity of the combinatorial film libraries, which may determine their physical properties. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Material libraries; Luminescent properties; Optical properties

1. Introduction

The combinatorial approach, in which the synthesis and screening of libraries with a large number of different organic molecules are implemented, has been widely used for the drug discovery [1]. Recently, Xiang and his colleague [2] pioneered the application of this approach to the discovery of new solid-state inorganic materials with desired properties. Combining combinatorial physical/lithography masks with thin film synthesis technique, integrated material chips with a large number of spatially defined different compounds are generated and screened [2]. The combinatorial technique can be widely used in materials science to increase the rate of new material discovery and optimization by several orders of magnitude.

During the last few years special interest has been devoted to create new nanocrystals of metals or compounds in SiO₂ by implantation, which may exhibit specific optical emission properties and be interesting for optoelectronic applications [3,4]. Implantation of elements such as Si [5], Ge [6], C [7], Ga and N [8] has been reported, which yields different luminescent prop-

erties. Our first application of combinatorial approach in ion implantation is intended to increase greatly the efficiency of sample synthesis and the possibility of novel nanocrystal formation, which may yield higher energy emission meeting the needs of high density optical storage.

In-depth study of the materials libraries is in some respects restricted by the difficulty in phase determination and composition inhomogeneity examination of the film libraries, which may determine their properties. In this paper, we report the application of the cathodoluminescence (CL) technique to identify local bonding environment that contributes to the luminescent properties, and the first application of Rutherford backscattering spectrometry (RBS) and proton elastic scattering (PES) method to determine the depth-resolved ion distribution of the combinatorial ion implanted samples.

2. Experimental

Boron doped<100>single crystal silicon wafers with ~ 400 nm SiO₂ on them were used for the implantation. Several elements, C, Ga, N, Pb, Sn and Y, were selected for implantation. The energies for the implantation were 40–80 KeV and each ion dose is about $1 \times 10^{16} \text{ cm}^{-2}$, depending on ion species. The ion beam

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impinged on the substrate through a set of physical masks, of which the combination of ion species is arranged in a similar way as described in [2]. The generated material chip (library) was subsequently thermally treated at 800°C for 30 min in a flowing Ar atmosphere, and was further characterized by CL, RBS and PES analysis.

The cathodoluminescence measurement system capable of producing beam current of 1–3 μA was employed to this study. RBS analysis was performed on the 4-MeV pelletron by using 2 MeV $^4\text{He}^+$ beams at a scattering angle of 170°. The energy resolution of the detector is about 16 KeV, and the total dose of $^4\text{He}^+$ was 3 μC .

3. Cathodoluminescences of materials libraries

Fig. 1 shows a material chip (library) of 64 different samples generated by ion beam implantation and six masking combinations, imaged under natural lighting. The different colors on various sample sites may originate from specific light reflections and interference from different interfaces.

We also conducted CL measurements of the material chip with various electron-impinging voltages. As the material chip is exposed to an electron beam irradiation of 5 kV, 1 μA , we can easily distinguish the implanted samples from the pristine substrate. Most samples are of blue emission, and differences in color and intensity of emitting light from the samples can be observed by naked eye. Yellow-green color from C-implanted samples and violet-blue from Sn-implanted samples are observed under 2 KeV electron bombardment, with some major CL peaks revealed in Table 1.

As evident in Table 1, the blue (450 nm) luminescent band is observed in all samples, and this is commonly observed in pristine SiO_2 and amorphous SiO_2 or silica, which is thought to be ascribed to the oxygen vacancy or E' center and the two-fold-correlated silicon center

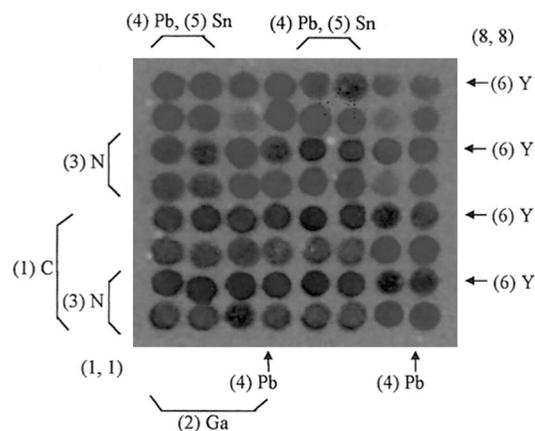


Fig. 1. An image of the ion implanted silicon-based material chip with a library of 64 samples prior to annealing under white lighting. The silicon wafer is $25 \times 25 \text{ mm}^2$ and each sample site is of 2 mm diameter. Indicated elements and braced numbers corresponds to the implanted ion species and their implantation sequences, respectively. Different implantation conditions for various elements are described as: (a) C, 50 KeV, $5 \times 10^{16} \text{ cm}^{-2}$; (b) Ga, 80 KeV, $1 \times 10^{16} \text{ cm}^{-2}$; (c) N, 50 KeV, $1.5 \times 10^{16} \text{ cm}^{-2}$; (d) Pb, 80 KeV, $1.5 \times 10^{16} \text{ cm}^{-2}$; (e) Sn, 70 KeV, $1 \times 10^{16} \text{ cm}^{-2}$; (f) Y, 65 KeV, $1 \times 10^{16} \text{ cm}^{-2}$.

[9]. CL measurements for the sample S(Ga, N) did not show any evidences for the existence of GaN crystals in SiO_2 , possibly because N diffuse through the film either to escape into the air or form $\text{Si}_3\text{O}_x\text{N}_y$, which can also be proved by non-existence of N determined by PES measurements.

All samples implanted with C look more or less yellow-green color. The S(C) exhibits a weak additional emission peaked 555 nm. The presence of C in the host is hopefully to induce the formation of a C-cluster, silicon carbide or silicon oxycarbide nanoparticles, which is of great interest because of the shift in luminescent emission towards higher energies compared to Si nanocrystals in SiO_2 with $\sim 680 \text{ nm}$ peak emission, when emissions in the violet range are expected. Indeed, the C can react with O in SiO_2 to form CO and/or CO_2 . It is assumed that the reduced Si can react with C to form silicon carbide or silicon oxycarbide when there is an access of C in SiO_2 .

Co-implantation of C and Ga in SiO_2 induce a strong emission peaked at $\sim 570 \text{ nm}$, even followed by Pb and Sn implantation. The Ga can react with SiO_2 to form Ga_2O_3 , a phosphor usually crystallized in highly anisotropy crystal structure [10]. From the evident diffusion of Ga to the C-peaked nearby region after annealing, one may deduce that C implantation would have induced the formation $\text{Ga}_x\text{Si}_y\text{O}_3\text{C}_x$, which is attributed to bonding impetus between Ga and C in SiO_2 rather than to the strain induced by implantation damage.

Fig. 2 shows a comparison of CL spectra for S(Pb, Sn, N) and the pristine substrate with various electron

Table 1
Characteristic CL spectra for the selected samples under 2 KeV electron bombardment

Sample	Dominant peak position (nm)	
S(C)	450	555 (0.10) ^a
S(N)		450
S(Ga, C)	450	570 (0.56) ^a
S(Ga, N)		445
S(Ga, Pb, C)		450 567 (0.60) ^a
S(Ga, Pb, Sn, C)	415 (0.75) ^a	450 565 (0.60) ^a
S(Pb, Sn, N)	405 (1) ^a	450
S(Pb, N)	435 (0.6) ^a	450

^a The data in the bracket indicates normalized emission intensity relative to $\sim 450 \text{ nm}$.

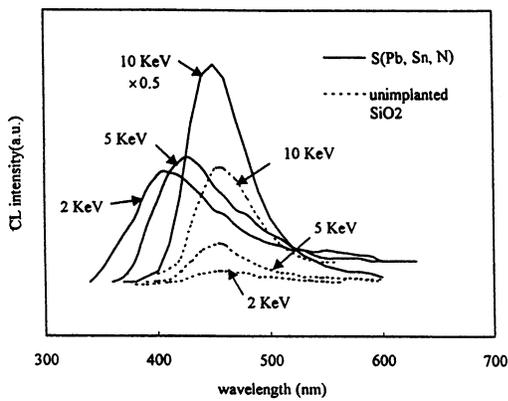


Fig. 2. Cathodoluminescence spectra of S(Pb, Sn, N) and unimplanted SiO₂ at various electron energies. The spectra were measured at the room temperature.

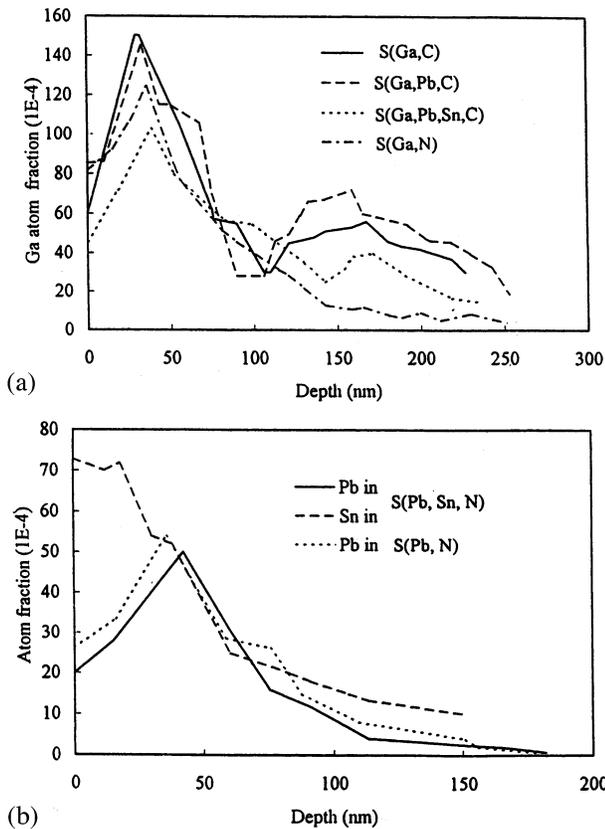


Fig. 3. Ion concentration depth-profiles determined from the RBS measurements for the material chip. (a) Ga profiles for S(Ga, C), S(Ga, Pb, C), S(Ga, Pb, Sn, C) and S(Ga, N); (b) Profiles of Pb and Sn for S(Pb, Sn, N) in comparison with Pb profiles for S(Pb, N).

energies. The band peak shifts to lower wavelength region as the beam energy decreases, with peaks at 450, 422 and 405 nm corresponding to beam energies of 10, 5 and 2 KeV, respectively. We have calculated the energy loss during electron penetrating into SiO₂ and suggest that implantation of Pb and Sn in SiO₂ causes an increase of pair formation and higher energy CL. As the electron energy decreases, the region approaching the surface is largely excited and peak band shifts to higher energies,

that is obviously owing to the effects of Pb- and Sn-related luminescent centers in the material, which can match the ion distributions measured by RBS [Fig. 3(b)].

4. Ion depth-resolved profiling by RBS and PES

Ion analysis is also used to quantitatively determine the constitution and elucidate the interaction among implanted ions that may yield correlated specific luminescence. The ion concentration depth-profiles calculated with RUMP program are shown in the Fig. 3. The Ga profile of S(Ga, C) is peaked at 36 and 172 nm from the surface, corresponding atom fractions of 1.5 and 0.56%, respectively Fig. 3(a). The profiles of S(Ga, Pb, C) and S(Ga, Pb, Sn, C) also show two peaks of Ga concentration, located at nearly the same position with respect to that of S(Ga, C). Fig. 3 shows that Sn diffused to the surface of S(Pb, Sn, and N) is responsible for the higher energy luminescent emission when bombarded with lower energy electrons.

PES measurements of S(C), S(N) and pristine SiO₂ by using 3 MeV H⁺ beams at a scattering angle of 170° result that the concentration peak of C for S(C) is 4.12 at.%, calculated by using the proton elastic scattering cross section enhancement factors, given in [11]. The spectrum of S(N) as shown did not reveal any trace of N after annealing, and that can be accounted for by the N diffusion and N escape-out in SiO₂ during annealing. Our previous work shows that the cross sections of light elements C, N and O are enhanced for proton elastic scattering with energy > 2.5 MeV, therefore, the simultaneously profiling of N, C and O over a sufficient depth range in a heavy material can be readily accomplished [11].

5. Summary

We have successfully developed a combinatorial ion synthesis and ion beam analysis technique to study ion-implanted material libraries, and significantly increased the efficiency of sample synthesis and analysis. Panchromatic imaging of optical properties combining with element profiling for material chip (library) can be used to screen some optical properties. Most important of all, our approach can be directly used to characterize nondestructively and rapidly the composition and the inhomogeneity of combinatorial film libraries.

Acknowledgements

This work is supported by the Chinese National Science Foundation under Contract No. 19875075, and K. C. Wong Educational Foundation.

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