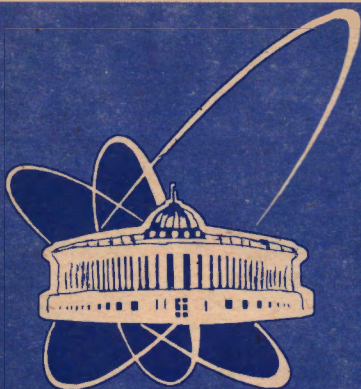


97-184



СООБЩЕНИЯ
ОБЪЕДИНЕННОГО
ИНСТИТУТА
ЯДЕРНЫХ
ИССЛЕДОВАНИЙ

Дубна

E14-97-184

A.P.Kobzev, O.A.Nikonov, M.Kulik*, J.Zuk*,
H.Krzyżanowska*, T.J.Ochalski*

ELEMENT DEPTH PROFILES OF POROUS SILICON

*Institute of Physics, Maria Curie-Skłodowska University, Lublin, Poland

1997

1. INTRODUCTION

Porous silicon has been the subject of intensive investigations since the initial demonstration of efficient visible photoluminescence in this material by L.T. Canham in 1990 [1]. The progress in research on porous Si was reviewed recently in [2,3]. Emission from porous Si is completely different from that observed in bulk crystalline Si, where the weak near-infrared luminescence associated with the indirect band gap of 1.1 eV has been known for a long time. For porous silicon, a large "blue" shift of the fundamental absorption edge has been reported. The spectacular optical properties of porous silicon are generally attributed to the spatial confinement of photo-excited carriers in nanometer-sized Si quantum wires or dots [1-3].

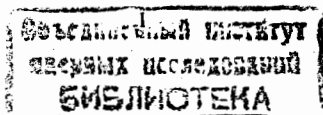
There are however, some other mechanisms of light emission in porous silicon. One of them has been linked to the E' centre in SiO₂ (an oxygen vacancy with an unpaired electron), and which is proposed to explain the strong blue emission observed in porous silicon when excited with ultraviolet light or protons [4]. It would be interesting, therefore, to estimate the oxygen content in a large (up to 1000 m²/cm²) surface of porous silicon.

2. EXPERIMENT

The samples used in a present experiment were prepared from p-type (111) silicon wafers of 10 Ω·cm resistivity. The porous layers were formed by anodization in a 48% HF-ethyl alcohol solution at a current density of about 20 mA·cm⁻². This technology of preparing porous silicon was described in [4]. The thickness of the porous layer was about 5 μm, as determined by interferometric microscopy.

Both non-destructive nuclear methods of ERD (Elastic Recoil Detection) and RBS (Rutherford Backscattering Spectroscopy) were used in the investigation of the depth element profiles in porous silicon. The measurements of RBS and ERD spectra were carried out at the EG-5 accelerator at the Frank Laboratory of Neutron Physics.

In the RBS experiment, the detector was positioned at a scattering angle of 170° with respect to the incident beam. The surface of the sample was tilted to the ion beam at a 60° angle. The detector resolution was 15 keV for 5.5 MeV α-particles. We overcame the difficulties of the RBS method in the investigations of the concentration of the light element (O) along with the heavier (Si) and used, in this case, the nuclear reaction ¹⁶O(α,α)¹⁶O to profile the oxygen directly [5]. The elastic nuclear resonance at 3.045 MeV is particularly suitable because it has a large back scattering cross section (17 times greater than for Rutherford scattering) and the resonance width is about 10 keV. The measurements have been performed in a such way that the energy of the



incident beam of ${}^4\text{He}^+$ ions was changed in small increments in the range from 3.04 MeV to 3.20 MeV. The backscattering spectra were collected for all energies. Thus, the resonance shifted from the surface to 5000 nm for the highest energy and we measured the oxygen profile in detail over the range of the depth above.

The ERD spectra were investigated for both porous and crystalline silicon. The 2.5 MeV ${}^4\text{He}$ ions were incident on a solid target at an angle of 15° with respect to the surface of the sample. The scattered ${}^4\text{He}^+$ ions were absorbed in stopper aluminium foil of $9.5\mu\text{m}$ thickness. In contrast, the recoiling nuclei (protons) lost only part of the full energy and were collected by a detector positioned at a laboratory scattering angle of 30° away from the direction of incidence.

3. RESULTS AND DISCUSSION

The typical spectra of ${}^4\text{He}$ ions scattered from the sample of porous silicon are presented in Fig.1 for two initial energies. The peak of the resonantly scattered ${}^4\text{He}^+$ particles rides over the background non-resonant scattering from oxygen. This

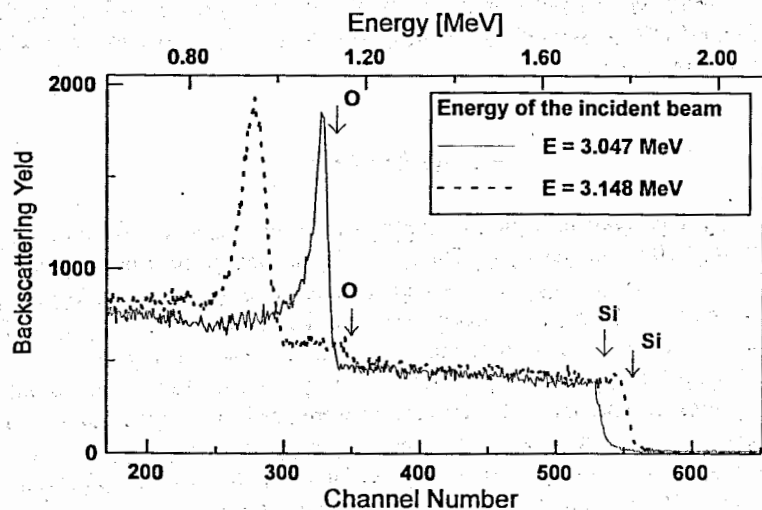


Fig. 1. Spectra of ${}^4\text{He}^+$ backscattered by a porous silicon sample.

background, in turn, sits on top of the continuum of the elastic scattering by silicon nuclei in the porous layer of the investigated sample.

The peak for the 3.047 MeV ${}^4\text{He}$ ions has a sharper right edge because the resonance partially entered the target in this case. A shift to the depth of the peak oxygen resonance by increasing the initial energy of the bombarding particles is observed since the ${}^4\text{He}$ ions reaches of the resonance energy at increasing depths. A

square of the peak is proportional to the oxygen atom concentration for the given depth.

In the spectra, one can see the yield of ${}^4\text{He}$ ions scattered by Si atoms. The background for the spectral regions from the surface layers is absent in this case. The element concentrations are obtained with help a computer code [6] after modelling all spectra using one joint model of the sample.

The ERD spectra obtained for the crystalline silicon and porous silicon samples are shown in Fig.2. In the spectrum for crystalline silicon, one can see a peak near

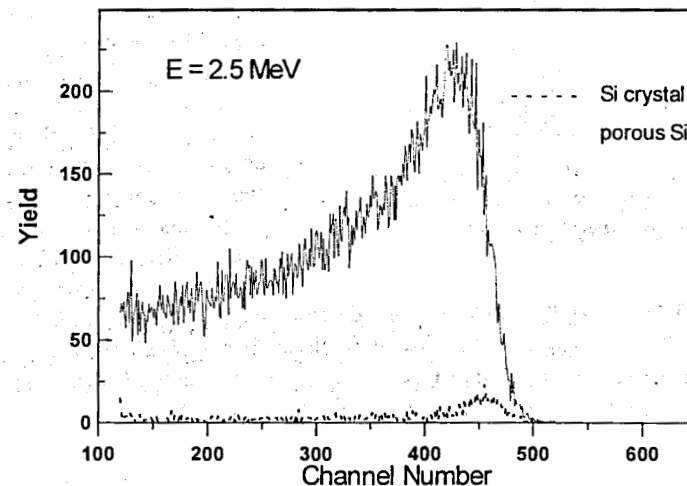


Fig. 2. ERD spectra of porous and crystalline Si

channel number 460. The yield of this peak is very small, as compared to the one for the porous silicon layer. This means that the hydrogen atoms are present only at the surface of the silicon. Since porous silicon has the vast specific surface, the yield of the recoiling hydrogen atoms for the porous sample is substantially more than for crystalline silicon and the depth profile extends to the whole depth available for the measurement.

The depth profiles of the different elements and pores in the porous silicon layer were calculated in two steps. In the first step, the depth profile of hydrogen in the porous silicon was determined on the basis of the ERD spectrum. Then these data were used in the calculations of the depth profiles of other elements (Si, O) and pores by modelling twelve RBS spectra with the help of a computer code [6]. These results are shown in Fig. 3. A special element was included in the model of the sample which attributed with the pores. It did not scatter He ions and had very small stopping cross-sections. This procedure gives the possibility to account the presence of pores in the solid with the first approximation only.

The concentration of Si atoms is the smallest ($\sim 20\%$) in the subsurface region

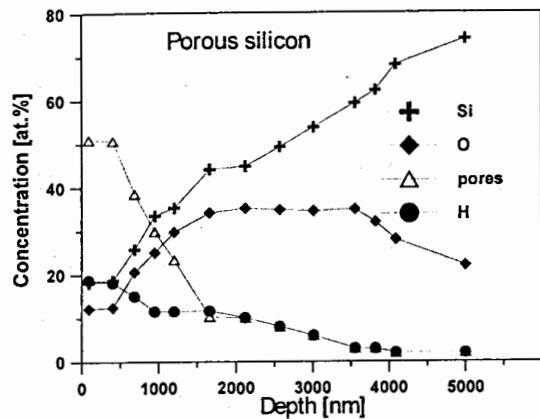


Fig. 3. Depth profiles of hydrogen, oxygen, silicon, and pore concentrations in porous Si, as determined from RBS and ERD measurements.

which are present in porous silicon after anodization, probably, appear as H_2O .

Thus, the performed investigation of depth profiles of all elements and pores in porous silicon strongly indicate, that there are sufficient amounts of oxygen to explain the spectrum of luminescence by excitation of the E' centre in SiO_2 .

References

1. L.T. Canham. Silicon quantum wire array fabrication by electrochemical and chemical dissolution of wafers. *Appl. Phys. Lett.* **57** (10), 1046 - 1051 (1990).
2. Y. Kanemitsu. Light emission from porous silicon and related materials. *Phys. Rep.* **263** (1), 1-91 (1995).
3. G.C. John and V.A. Singh. Porous silicon: theoretical studies. *Phys. Rep.* **263** (2), 93-151 (1995).
4. J.Žuk, R. Kuduk, M. Kulik, J. Liškiewicz, D. Maćzka, P.V. Zhukovski, V.F. Stelmakh, V.P. Bondarenko and A.M. Dorofeev. Ionoluminescence of porous silicon. *J. Lumin.* **57**, 57-60 (1993).
5. L.P.Chernenko, A.P.Kobzev, D.A.Korneev and D.M.Shirokov. Backscattering methods possibilities for precise determination of oxygen profile in oxide films by use of the elastic resonance in reaction $^{16}O(^4He, ^4He)^{16}O$ at 3.045 MeV of 4He . *Surface and Interface Analysis*. vol.18, 585-588 (1992).
6. V.Bogac and D.M.Shirokov. New computer iterative fitting program DVBS for backscattering analysis. *Nucl. Instrum. and Meth.* **B85**, 264-267 (1994).

Received by Publishing Department
on June 5, 1997.

and gradually increases with depth up to 75% (Fig. 3). The porous Si layer is non-homogeneous, with a porosity (after anodization) ranging from about 50% close to the surface to less than 10% at a depth of 1600 nm and slowly decreases to almost zero at 4000 nm. The concentration of oxygen is less than 30% for whole thickness of the porous silicon layer. The C_{Si}/C_O ratio increases from 1.2 at the surface to 3.2 with increasing depth to 5000 nm. Therefore, it can be assumed that the Si wires in porous silicon are covered with silicon oxide layers. Moreover, the hydrogen atoms,

Кобзев А.П. и др.

E14-97-184

Профильный элементный анализ пористого кремния

Профильный элементный анализ пористого кремния был проведен на ускорителе Ван-де-Граафа с энергией ионов $^4He^+$ в диапазоне от 2 до 3,2 МэВ. Применение взаимодополняющих методик RBS, ERD и ядерной реакции $^{16}O(\alpha, \alpha)^{16}O$ при энергии 3,045 МэВ позволило получить:

- 1) точное распределение кремния, кислорода и водорода по глубине,
- 2) распределение относительной концентрации пор.

Концентрация кислорода в пористом кремнии доходит до 30 %, что позволяет предположить наличие окисла кремния в порах и объяснить сдвиг люминесценции в голубую область.

Работа выполнена в Лаборатории нейтронной физики им.И.М.Франка ОИЯИ.

Сообщение Объединенного института ядерных исследований. Дубна, 1997.

Kobzev A.P. et al.

E14-97-184

Element Depth Profiles of Porous Silicon

Element depth profiles of porous silicon were measured on the Van-de-Graaf accelerator in the energy range of $^4He^+$ ions from 2 to 3.2 MeV. Application of complementary RBS, ERD and $^{16}O(\alpha, \alpha)^{16}O$ nuclear reaction methods permits us to obtain:

- 1) the exact silicon, oxygen and hydrogen distribution in the samples,
- 2) the distribution of partial pore concentrations.

The oxygen concentration in porous silicon reaches 30 %, which allows one to assume the presence of silicon oxide in the pores and to explain the spectrum shift of luminescence into the blue area.

The investigation has been performed at the Frank Laboratory of Neutron Physics, JINR.

Communication of the Joint Institute for Nuclear Research. Dubna, 1997.