ELSEVIER

Nuclear Instruments and Methods in Physics Research B 190 (2002) 339–344

NIM B
Beam Interactions with Materials & Atoms

www.elsevier.com/locate/nimb

Sub-micron channeling contrast microscopy on reactive ion etched deep Si microstructures

E.J. Teo [a], M Alkaisi [b], A.A. Bettiol [a], T. Osipowicz [a,*], J. Van Kan [a], F. Watt [a], A. Markwitz [c]

[a] *Department of Physics, Research Centre for Nuclear Microscopy (RCNM), National University of Singapore, Lower Kent Ridge Road, Singapore 119260, Singapore*

[b] *Department of Electrical and Electronic Engineering, University of Canterbury, Private Bag 4800, Christchurch, New Zealand*

[c] *Institute of Geological & Nuclear Sciences Ltd., Rafter Laboratory, P.O. Box 31-312, Lower Hutt, New Zealand*

Abstract

High aspect ratio microstructures with compositional inhomogeneity have always been a challenge for broad beam analysis due to the shadowing effect. In the present work, characterization of reactive ion etched (RIE) Si microstructures is carried out using channeling contrast microscopy with a sub-micron beam spot size. An annular detector is used to minimize surface topography effects. The etch damage introduced by the RIE process on Si is determined from channeling measurements. It is found that crystallinity is preserved in the etched trenches, indicating that little damage was inflicted to the crystal lattice by the RIE process. In the axial channeling position, the Si background signal from the substrate is reduced and sensitivity to the light elements detection is increased. This allows quantitative analysis of the composition in the masked regions and etched trenches. The channeled spectrum in the masked regions reveals the presence of a siliconoxyfluoride layer. No F is observed in the etched trenches. © 2002 Elsevier Science B.V. All rights reserved.

PACS: 07.78.+s; 61.85.+p; 81.65.Cf
Keywords: Reactive ion etched; Channeling contrast microscopy; Topography; Crystal quality; Composition

1. Introduction

Often, high reflectivity of bare silicon limits the collection efficiency of the solar cells. Therefore in order to improve solar cell performance, the surface reflectance and transmission has to be reduced. This can be done by coating the surface with antireflective layers [1] or by texturing the Si itself [1,2]. Texturing involves roughening of the silicon substrate to increase light absorption through multiple reflections. This results in bigger effective surface area and better collection efficiency. Wet etching, laser grooving and reactive ion etching (RIE) are common techniques used to obtain a textured surface.

Characterization of these patterned microstructures is necessary in order to understand and optimize the etching processes. However, not many techniques offer the spatial resolution needed to

* Corresponding author. Tel.: +65-772-6745; fax: +65-777-6126.
E-mail address: phyto@nus.edu.sg (T. Osipowicz).

PII: S0168-583X(01)01255-1

investigate the microstructures. Angular resolved X-ray photoelectron spectroscopy has been used to provide chemical information of the masked regions and sidewalls [3]. However, this approach only gives qualitative results. In this work, we demonstrate the use of sub-micron channeling contrast microscopy (CCM) to provide laterally resolved information of the crystal quality and composition of the RIE textured Si.

2. Experimental procedures

A silicon ⟨1 0 0⟩ substrate was covered with SiO_2 and then 40 nm thick of NiCr film was deposited by thermal evaporation. Patterns of the required texture were first defined using optical lithography, by exposing photoresist coated substrates through a mask containing arrays of holes of 5 μm diameter. After exposure of the samples and development of the resist, the sample was soft baked at 95 °C for 30 min. The NiCr film is wet etched for 30 s to allow subsequent RIE through the holes. The required pattern is then transferred to the NiCr metal mask. An SF_6/O_2 gas mixture is utilized for the RIE process. The purpose of the oxygen addition during etching is to form an SiO_xF_y layer to passivate sidewalls and improve the aspect ratios. The following RIE conditions had been used: SF_6 gas flow rate 100 sccm (standard cubic centimeter), electrode temperature 173 K, power density 0.45 W/cm^2, etch pressure 70 mTorr, and dc bias -161 V. An etch rate of 500 nm/min was achieved. The etching process resulted in creation of holes ranging from 7 to 10 μm depth and 5 μm width.

CCM [4] was performed at the nuclear microscopy facility at the National University of Singapore [5]. A $^4He^+$ ion beam of 1.6 MeV was focused down to a sub-micron spot size and scanned over a sample area of 48×48 μm^2 with typically 100 pA beam current. The collimators were set so that the divergence of beam was less than $0.2° \times 0.09°$. This condition provides reasonable channeling as the beam divergence is significantly less than the critical half angle of 0.4° in [1 0 0] silicon. Channeling RBS spectra were recorded with a 25 mm^2 annular detector of 22 keV resolution near 180° backscattering angle. The annular detector was used to minimize shadowing effects due to the surface topography. The targets were mounted on an eucentric goniometer with a 24 mm translational range for the x and y directions allowing rotations with a resolution of 0.025°. A large solid angle of 108 msr was used due to the limited current. The data was collected in list-mode, so that RBS spectra from arbitrary regions of the 256×256 pixel scans could be extracted off-line. A channeltron mounted at 20° to the surface was used for secondary electron imaging of the surface topography.

The sample morphology was characterized by scanning electron microscopy (SEM).

3. Results and discussion

Fig. 1(a)–(c) show the SEM micrographs of the cross-sectional, planar and glancing view of the high aspect ratio Si trenches. The cross-section SEM micrograph in Fig. 1(a) reveals a 'wine glass' etch profile, with 6 μm wide trenches extending 11 μm into the substrate, surrounded by broader trenches of 13 μm diameter with 4 μm depth. This latter feature is undesirable and its origin is not fully understood yet. It might be due to a two step etch process, i.e. an isotropic phase followed by a directional etching step. The isotropy of the etch profile can be explained by the dominance of the chemical etching over the dry etching. This is common for Si etching in F atom-rich plasmas due to the spontaneous reaction of F with Si. The O_2 content has also been shown to have a strong effect on the directionality of the etch profile [3]. Inadequate oxygen for sidewall passivation may result in fluorine attack and concomitant etching.

Fig. 2 shows the ion beam induced secondary electron image of the Si microstructures. The map reveals the topographic information of the textured Si obtained with sub-micron beam resolution. Henceforth, region a will be referred to as etched trenches, b as overetched regions and c as masked regions.

Fig. 3 shows the CCM map of the microstructures obtained from the first 2 μm layer, in the [1 0 0] direction. The grayscale of the image corresponds to the intensity of the channeled yield. In

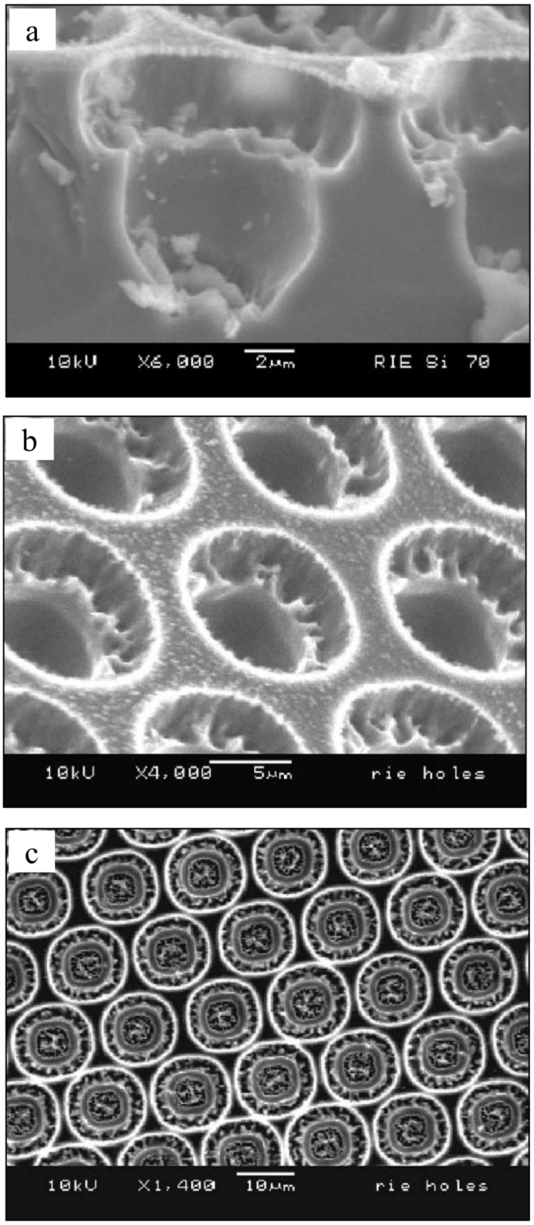

Fig. 1. SEM micrographs of the RIE Si microstructures : (a) cross-sectional view, (b) glancing view, (c) planar view.

order to determine the crystallinity of the deep trenches, it is important to ensure that there is no shadowing effect for the outgoing particles due to surface elevations. This would have caused a substantial reduction in the energy of the particles emerging from the deep trench for a given depth in

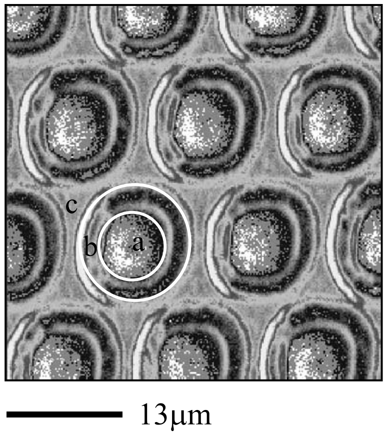

Fig. 2. Ion induced secondary electron image of surface topography. Regions a correspond to etched trenches, regions b to overetched regions and regions c to masked regions.

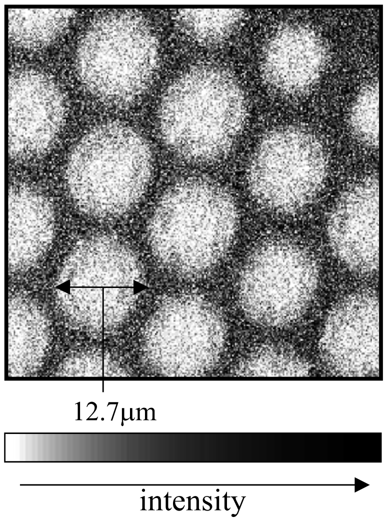

Fig. 3. CCM map of the RIE Si microstructures.

the sample and result in distortion of the channeling measurements. The contrast patterns reveal symmetric and homogeneous microstructures with no topographic effects. The fact that these contrast patterns disappear in the random alignment further confirms that the variation in yield is solely due to channeling effects. Bright areas of low backscattered yield can be observed in the 6.6 μm etched trenches. This suggests that the crystallinity is preserved after the RIE process. There is an increased yield from the overetched regions. The masked regions appear much darker than the etched regions due to the amorphous oxide coverage. Therefore, individual regions of interest can be extracted for analysis from the high resolution CCM map.

To investigate the RIE effect on crystal quality and composition of the silicon substrate, the channeled spectrum is extracted from the 6.6 μm etched trenches (as indicated by a), overetched regions (b) and masked areas (c) separately. These are compared with the channeled and random spectrum of a pure silicon sample in Fig. 4. The channeled spectrum of etched Si trenches is similar to that of pure Si, indicating good channeling in these regions. Quantitatively, it is found that the χ_{min} values are 5.1% and 7.4% for the pure silicon and etched regions respectively. Therefore, it can be concluded that the RIE process introduces only slight damage to the silicon crystal structure. The etch damage depends mainly on the energy and mass of the ions used in the dry etching process. This suggests that the etching process is dominated by wet etching instead of physical etching. No fluorine is observed in these trenches, indicating the almost complete removal of the SiF_4 by the energetic impinging ions.

The channeled spectrum from the masked regions reveals the presence of a thin passivation layer of siliconoxyfluoride deposited on top of the silicon oxide. The axial channeling reduces the silicon background signals and increases the sensitivity to the light elements detection. After subtraction of the nearly linear background from the silicon substrate, it is possible to determine the composition and thickness of the surface passivation layers. From RBS simulations using SIMNRA [6], the thickness of the SiO_2 is found to be about 212 nm. It is passivated with 60 nm of siliconoxyfluoride. This suggests that the NiCr mask was etched away during the RIE process, exposing the underlying SiO_2 layer to the SF_6/O_2 plasma. The F* radicals quickly reacted with SiO_2 to form a layer of SiO_xF_y. The absence of the NiCr mask in

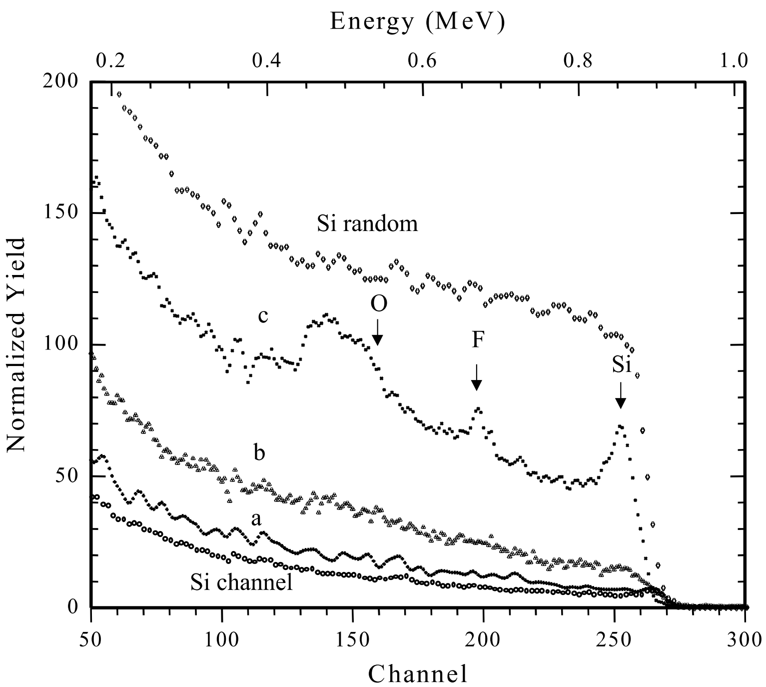

Fig. 4. Channeled spectrum of (a) etched trenches, (b) overetched regions and (c) masked regions. Channeled and random spectra of Si are plotted for comparison.

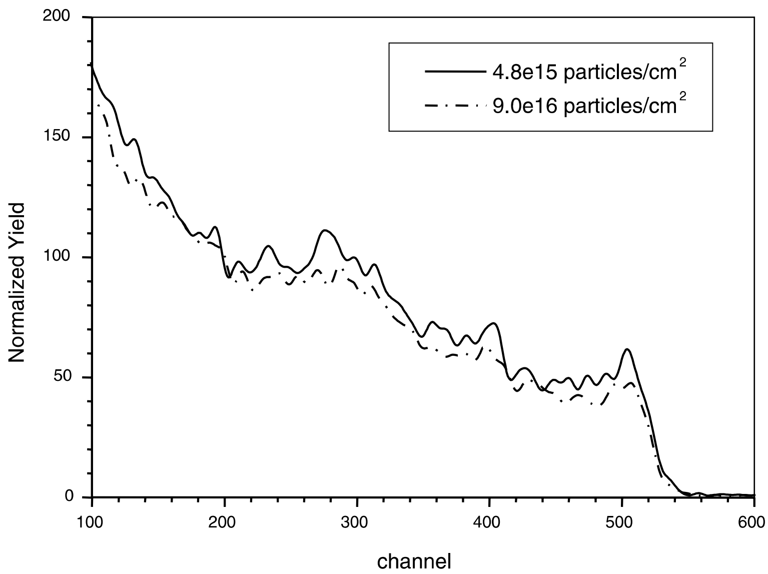

Fig. 5. Comparison of the normalized spectra collected at 4.8×10^{15} and 9×10^{16} He^+/cm^2.

Fig. 1(a) further confirms the complete removal of the mask in the etching process.

Fig. 4 shows that the normalized channeled yield in the overetched regions is about two times higher than that of the etched Si. The interpretation of this observation is a non-trivial task. In principle, the higher yield might be due to higher etch damage in these regions. However, this is unlikely since good crystallinity is observed in the etched trenches. The SEM micrographs in Fig. 1(a) and (b) show more roughness in these regions, especially at the diameter of 6.6 μm. This could be due to micromasking effects from the oxide layer that was on the surface. Therefore, a more likely explanation for the increase in yield could be the partial coverage of oxide micromask on the Si substrate.

The extent of damage caused by the He ion beam during analysis has been investigated as well. This can be done by comparing the spectra collected for the first and last 10% of the ion dose in a long CCM run (see Fig. 5). These channeled spectra, taken at a average doses of 4.8×10^{15} and 9.0×10^{16} He^+/cm^2, are very similar, confirming that damage accumulation is negligible on the sample during the collection time. It was estimated by Ingarfield et al. [7] that significant lattice damage happens when He^+ fluence exceeds 6.2×10^{17} He^+/cm^2. Therefore, CCM is a reliable technique for studying the etch damage on crystal lattice.

4. Conclusions

Sub-micron CCM has been successfully employed to provide laterally resolved information of crystal quality and composition across RIE silicon microstructures. By selecting the data from the etched regions, it is possible to assess the etch damage introduced by the RIE process. The slight increase in yield after etching indicates that low damage has been inflicted on the crystal lattice by the RIE process. This suggests the dominance of chemical etching over the dry etching process. RBS measurements from the masked regions showed the presence of a thin layer of siliconoxyfluoride of about 60 nm deposited on the 212 nm SiO_2 layer. This information is useful for future optimization of the etching conditions to achieve anisotropic microstructures with minimal etch damage. Therefore, CCM is a powerful technique for characterization of patterned microstructures without any sample preparation, in a non-destructive manner.

Acknowledgements

This work was partly funded by a research contract to the New Zealand Foundation for Research, Science and Technology (UOCX9905 'Nano-engineered Materials for Optics and Electronics').

References

[1] S. Winderbaum, O. Reinhold, F. Yun, Solar Energy Mater, Solar Cells 46 (1997) 239.
[2] H.F.W. Dekkers, F. Duerinckx, J. Szlufcik, J. Nus, Opto-Electronics Rev. 8 (4) (2000) 311.
[3] G.S. Oehrlein, K.K. Chan, M.A. Jaso, G.W. Rubloff, J. Vac. Sci. Technol. A 7 (3) (1989) 1030.
[4] M. Breese, D. Jamieson, P. King, Materials Analysis Using Nuclear Microprobe, John Wiley & Sons, New York, Chapter 5, p. 208.
[5] D.J.W. Mous, R.G. Haitsma, T. Butz, R.H. Flagmeyer, D. Lehmann, J. Vogt, Nucl. Instr. and Meth. B 130 (1997) 31.
[6] M. Mayer, SIMNRA User's Guide, Technical Report IPP9/113, Max Planck Institut für Plasmaphysik, Garching, Germany, 1997.
[7] S.A. Ingarfield, C.D. McKenzie, K.T. Short, J.S. Williams, Nucl. Instr. and Meth. B 191 (1981) 521.