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Edge supported amorphous silicon membranes for diffraction studies

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Abstract

Edge-supported membranes of pure, non-porous, amorphous silicon have been prepared by ion implantation and chemical attack. Analysis by elastic recoil detection showed that impurities levels for oxygen and hydrogen are well below 0.1 at.% except in a thin layer at the etched surface. Raman spectroscopy confirmed the amorphous nature of the samples as well as the difference between as-implanted and thermally annealed samples. These samples were later used for X-ray diffraction measurements with the goal of determining reliably the radial distribution function of amorphous silicon with high resolution. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

The radial distribution function (RDF) is one of the most important properties of an amorphous material since it relates directly to the atomic structure [1]. It is essential that the RDF be known if a thorough understanding of the nature of the amorphous structure itself or that of its structural relaxation and point defect phenomena is to be reached. Experimentally, the RDF is determined by a Fourier transform of the diffracted intensity of X-rays or neutrons and such a measurement

obviously requires a sufficient amount of material. In this paper we describe how to make amorphous silicon (a-Si) samples for an experiment aimed at obtaining the RDF of a-Si but the procedure can of course be modified for other materials.

Amorphous silicon is an important model system for all amorphous materials because its basic building block is a single silicon atom. Its structure, and its similarities and differences with crystalline silicon (c-Si), should therefore be relatively easily understood and relate directly to the role of disorder on its (electrical, optical, mechanical, thermal, and so on) properties. Surprisingly, the RDF of pure, non-porous, amorphous silicon is not reliably known in spite of repeated efforts [2–7]. In fact, a number of papers with model calculations

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on the structure of amorphous silicon [8] compare the calculated RDF with one experimentally determined on amorphous germanium [9].

The paucity of reliable information regarding the RDF of a-Si stems from the difficulty of obtaining sufficient material of high purity and good homogeneity for the diffraction experiment. Plasma- or chemical vapour deposited hydrogenated a-Si can be of very high quality but contains of course a few at.% of hydrogen. Amorphous silicon made by sputtering typically contains a similar amount of the sputtering agent, whereas a-Si made by vacuum evaporation tends to peel off the substrate even before the layer thickness reaches 1 μm . More importantly, almost all a-Si made by deposition techniques contains voids [10] that may reach several nm in size and represent a volume fraction of several at.%, which means that a considerable fraction of the atoms sits at an internal surface and not in the bulk. The origin of the void structure may be related to the fact that every atom in the deposited a-Si was a surface atom during some stage of the deposition process. The best way to avoid the inclusion of the voids, therefore, is to prepare a-Si directly from the crystalline or liquid phase.

There are, as far as we can tell, four ways of making a-Si directly from the crystalline or liquid phase. Nano-indentation of crystalline silicon gives, upon sudden release, extremely small amounts of a-Si [11]. The amounts are so small that it is even difficult to establish its amorphous nature. Pulsed laser melting of c-Si can give, if the pulse duration and laser energy density are well chosen, pure a-Si but the layer thickness is only a few nm [12,13]. Ball milling yields large amounts of material but it generally contains so much iron that it is better to speak of amorphous alloys although some relatively pure a-Si has been reported [14]. That leaves ion implantation. MeV self-ion implantation typically gives up to a few micron of a-Si of very good reproducibility. The layer thickness can be increased to 12 μm by increasing the implantation energy to 30 MeV or so. It has been shown conclusively by small angle X-ray scattering that a-Si prepared this way is indeed free of nano-voids [15], even though its density is a little less than that of c-Si [16,17]. In this paper, we

describe the preparation and characterization of a-Si samples suitable for use in an X-ray diffraction experiment by multi-MeV ion implantation.

2. Ion implantation

The ion implantation schedule is based on the famous recipe of D.C. Jacobson for the preparation of 2 μm thick a-Si layers [18]. Reproducibility is achieved by cooling the silicon wafer to liquid nitrogen temperature during the ion implantation, by maintaining a power deposition of less than a few W/cm^2 , and by an implantation dose that exceeds the threshold for amorphization by a factor of five. The recipe calls for three successive implantations of 5×10^{15} Si ions/ cm^2 , namely at 500 keV, 1 and 2 MeV. The amorphization takes place most efficiently near the end-of-range, and a logical extension of this recipe for thicker a-Si layer would be to simply add higher energy ion implantations, where each additional implantation step would add a fraction of a μm a-Si (the buried interface between a-Si and c-Si would go a bit deeper at each implantation). The ion doses at each energy were estimated by aiming for a similar nuclear energy deposition as in the end-of-range of the 2 MeV implantation, as calculated by TRIM [19]. This led to the implantation sequence as shown in Table 1 which calls for a total implantation dose of 8.3×10^{16} Si ions/ cm^2 at energies up to 27 MeV. Readers wishing to see the TRIM simulation of this implantation sequence are invited to do the calculations themselves.

A potential concern of this method is that the multi-MeV ions passing through the a-Si that already exists somehow induce crystallization or structural relaxation at or near the surface. This could possibly occur as a result of the large electronic energy loss of these ions. Raman spectroscopy of the ion-implanted surface did not show any sign of this happening. Another concern is the possibility that thin c-Si layers remain between the end-of-range amorphized layers of the last and highest energy implantations, because at the higher energies the separation between the EOR becomes substantial. There was no way to test this other than by the actual X-ray diffraction

Table 1
Ion energies and doses used for amorphizing a 12 μm surface layer of c-Si

Ion Energy (MeV)	1.5; 2.0; 3.5	5; 7; 9	11.5; 14; 17; 20	23; 27
Fluence (Si ions/cm ²)	5×10^{15}	6×10^{15}	8×10^{15}	9×10^{15}

measurement. No evidence for c-Si remaining in between the a-Si layers was found, even in 12 μm thick samples that had been thermally annealed at 600°C for 1 h. (Any remaining c-Si seed would have grown to an easily observable crystallite by such a treatment [20].)

The sequence shown in Table 1 was used to fabricate a number of samples. Some were just a 1 cm² area of a slightly larger rectangular piece of undoped Cz, double sided polished c-Si of 100 μm thickness and these were meant for the X-ray diffraction experiments. Some were kept as-implanted; others were annealed in vacuum at 600°C for 1 h. The c-Si backing of these samples was removed as will be discussed in the next section. Other samples were made that were somewhat larger but required no removal of the backside. These were the (300 μm thick, single side polished) samples used in the small angle X-ray scattering experiments, mentioned in the introduction, that showed the absence of voids in this material.

3. Attack of the KOH

The X-ray diffraction measurement requires that there are no traces of c-Si exposed to X-rays during the measurement because such traces will introduce Bragg peaks that would have to be removed manually from the data. Therefore, the c-Si backing has to be removed and this was accomplished by a chemical etch. To this end, the sample was turned upside down and covered with a Teflon container filled with etching solution (20% KOH in water). The container had a small circular hole in the bottom, which was pressed against the c-Si back surface. A cross section of the container, viton and teflon o-rings, and the sample, is shown in Fig. 1. A series of concentric seals was used since a single o-ring gave unsatisfactory results: leakage between the surrounding hot water and the container occurred and furthermore, relatively large

strains accumulated at the single sealing surface which we suspect were responsible for enhanced etch rates around the perimeter of the o-ring. The only way to avoid enhanced etch rates at the o-ring was to use a flat teflon seal.

To facilitate etching, the c-Si starting material was only 100 μm thick and polished at both surfaces. A variety of materials could have been used as an effective etch stop [21], but this would have introduced two problems: first, the deep end of the thick a-Si layer would have to coincide exactly with the beginning (or rather, the near-surface side) of the etch stop and second, some of the etch stop material would inevitably be ion mixed into the a-Si. Instead, the etch speed in c-Si was determined precisely (1.2 $\mu\text{m}/\text{min.}$) and the temperature closely controlled to keep it constant at 80°C. The etch depth was essentially controlled by carefully timing the chemical attack. It was found that the etch rate of KOH in a-Si is about one-half that of the etch rate in c-Si [22,23], which helped a lot with the timing of the etch depth. In fact, during the etch, bubbles appear at a constant rate at the etched surface and a sudden decrease in the rate of bubble formation signals the arrival of the etch solution at the a-Si. The teflon container is then emptied and the sample removed and cleaned.

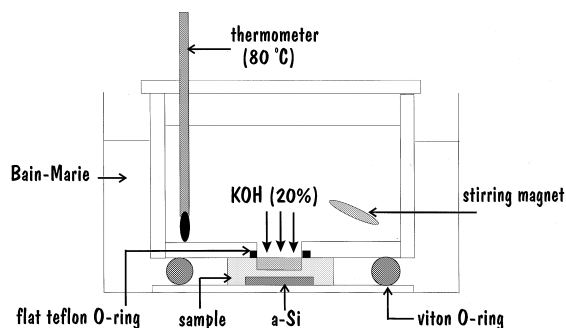


Fig. 1. Schematic cross section of the etching apparatus which shows the sample, the teflon container, and the seals. The entire apparatus was submerged in hot water (au bain Marie).

The end result of the chemical attack is a circular membrane of pure a-Si that is supported at the edges by the original c-Si sample. These membranes were found to be surprisingly robust; they survived additional ion beam bombardment and physical transport over many km. The thickness of the membranes is a bit less than that of the original a-Si layer because the etch always removes some of the a-Si. The thickness of each membrane was measured by determining the energy loss of MeV protons passing through the membranes. This was achieved by scattering MeV protons off a piece of Si into a surface barrier detector. The membrane was inserted between the Si piece and the detector and the apparent surface energies of the Rutherford backscatter spectrum with and without membrane were compared. It was found that all membranes had thicknesses between 9 and 11 μm . Because the density of a-Si is slightly less than that of c-Si, the a-Si membranes tend to buckle a little bit because they are larger than the diameter of the etched hole.

4. Chemical purity

Ion implantation of Si ions into c-Si undoubtedly can produce a-Si of the highest purity but there are two reasons that dictate that the purity of the samples should be verified. One, vacuum or beam problems during the implantation may introduce impurities near the surface and throughout the a-Si. Second, during the chemical attack at 80°C, impurities could conceivably diffuse into the a-Si back-surface. The chemical purity of the a-Si membranes was verified by elastic recoil detection of 35 MeV Cl ions incident 15° from the surface [24–27]. Both the front and the back-surface of an a-Si membrane were tested. Hydrogen recoils were separated from all other recoils by a stopper foil and detected by means of a surface barrier detector. All other elements were detected in the time-of-flight arm of the ERD chamber. In all cases, the outgoing recoils were collected at 15° from the surface; the angle between incident beam and detected recoils was 30°.

Analysis of the time-of-flight spectra and the hydrogen spectrum [28] leads to the data shown in

Fig. 2, which shows all impurities that could be detected at the etched surface. Since some surface roughness remains after the etch, the depth scale is only approximate. Substantial hydrogen and oxygen and some carbon and metallic impurities are observed at the surface and in the first 20 nm but well into the bulk all impurity levels drop to values below 0.1 at.% or the detection limit. The small signal attributed to metallic impurities is likely due to contamination of the etching solution from the chromel–alumel thermocouple. Since the X-ray measurement will probe the entire thickness of the sample (10 μm), the surface contamination is inconsequential. No metallic impurities were observed on the other surface of the membrane.

5. Structural relaxation and exposure to 60 keV X-rays

One key finding of the X-ray measurements [29] was that the two samples yielded RFD's that were much more similar than expected based on earlier attempts. This raised the question of possible relaxation by the multi-MeV ions passing through the surface or during the chemical attack, or possible relaxation or de-relaxation induced by the

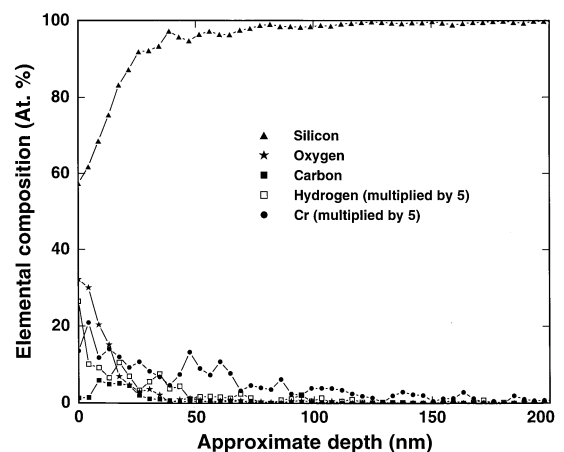


Fig. 2. Depth profiles of Si and all detected impurities at the KOH-etched back surface of an a-Si membrane. The depth scale is approximate because of surface roughness. The signals for H and Cr have been multiplied by a factor of 5 for clarity.

X-ray photons. We have therefore determined the Raman spectra at spots on the surface where the X-ray beam had hit the samples. The samples were illuminated with at most 100 mW from an Ar laser at a wavelength of 514.5 nm, focussed to a size of less than $0.1 \times 0.1 \text{ mm}^2$. The Raman system used included a double spectrometer equipped with a single-channel photon counting detector, which severely limits the quality of the spectra that can be obtained compared to CCD camera results. However, the spectra do indeed show a difference between the two samples.

Two measured spectra are shown in Fig. 3. The background was in fact larger than the signal and was removed. This was achieved by measuring the background of a c-Si sample, clipping the sharp peak at 521 cm^{-1} away, and smoothing. The smoothed curve was multiplied with a single normalization constant in order to obtain a signal that could serve as a background for the spectra measured on a-Si. This procedure is not entirely satisfactory and we are planning to undertake additional Raman measurements once the system is equipped with a CCD camera. Raman spectra measured immediately adjacent to the X-ray footprints could not be distinguished from those on the X-ray spot.

The peak positions of the TO-like band of the a-Si samples shifts from 474 ± 3 to $483 \pm 2 \text{ cm}^{-1}$

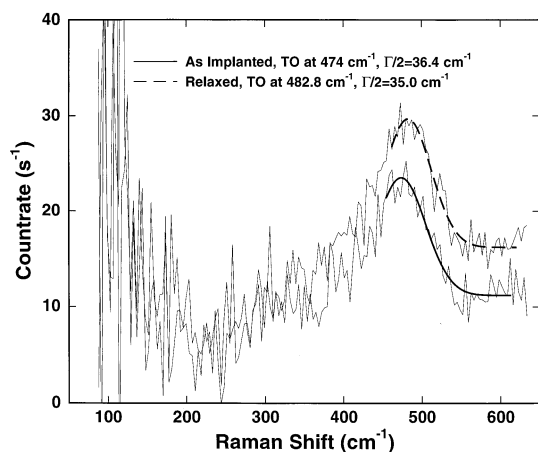


Fig. 3. Raman spectra of the a-Si membranes that were used for X-ray diffraction measurements. The Raman laser struck the samples at the same position as previously the X-ray beam.

upon annealing at 600°C , which corresponds very closely to values reported previously [30]. However, at the same time, the half-width at half maximum of the bands decreases only from 36.5 ± 4 to $35 \pm 3 \text{ cm}^{-1}$, while based on the literature, the widths were expected to decrease from about 42 to 34 cm^{-1} . The error in the values for the band widths is quite large and moreover, the band widths are more sensitive to errors in the background subtraction procedure than the peak positions. The error in the peak positions is also found to be small compared to the difference between the two peak positions. We tentatively conclude that all the dire straits mentioned in the first paragraph of this section did not materialize.

6. Conclusions

In conclusion, edge-supported a-Si membranes of $10 \mu\text{m}$ thickness have been made by a sequence of MeV ion implantations followed by a KOH chemical attack. The membranes are somewhat buckled and of good mechanical strength. The a-Si of the membranes is of high purity with less than 0.1 at.% contaminants and exhibits, within the limited resolution currently available, the same Raman spectrum as “normal” a-Si. Thermal annealing induces structural relaxation whereas prolonged exposure to X-rays from 13 to 60 keV does not significantly alter the Raman spectrum.

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