Characterization of amorphous silicon

Cite as: AIP Conference Proceedings **303**, 48 (1994); https://doi.org/10.1063/1.45528

R. A. Hakvoort, A. van Veen, H. Schut, et al.

CHARACTERIZATION OF AMORPHOUS SILICON

R.A. Hakvoort, A. van Veen and H. Schut,
Interfaculty Reactor Institute, Delft University of Technology, Mekelweg 15, NL–2629 JB Delft, The Netherlands,

M.J. van den Boogaard and A.J.M. Berntsen,
Utrecht University, Debye Institute, Dept. of Atomic and Interface Physics, P.O. Box 80000, NL–3508 TA Utrecht, The Netherlands,

S. Roorda[1] and P.A. Stolk,
FOM Institute for Atomic and Molecular Physics, Kruislaan 407, NL–1098 SJ Amsterdam, The Netherlands,

A.H. Reader,
Philips Research Laboratories, P.O. Box 80000, NL–5600 JA Eindhoven, The Netherlands.

ABSTRACT

S-parameter positron beam measurements have been done on several kinds of a-Si: Kr-sputtered a-Si, PECVD a-Si, MeV ion beam amorphized Si and a-Si grown in an MBE-system at a low deposition temperature. Kr sputtered a-Si becomes denser for higher Kr concentration. PECVD a-Si:H contains micro-cavities with a size depending on growth temperature. MeV ion beam amorphized Si contains 1.2 at.% small vacancies, which decreases upon annealing (relaxation) to 0.4 at.%. This effect can be mimicked by H-implantation and subsequent annealing, showing that at least some of the dangling bonds in a-Si are located at these vacancy-type defects. Finally positron measurements show that MBE-system grown a-Si contains large open-volume defects. The positron annihilation data are supplemented by data from some other techniques.

INTRODUCTION

The study of the annealing behaviour and the role of incorporated gases like H and noble gases in a-Si is interesting from both theoretical ('structure' of a-Si) and practical standpoint (solar cells, etc.). Dangling bonds in a-Si deteriorate the electrical properties of the material. The carriers are trapped at these bonds. On the other hand hydrogen may passivate these dangling bonds. Positrons are sensitive to electric charge and are therefore thought to be capable of probing these defects.

EXPERIMENTAL

Four types of a-Si have been examined:

1) a-Si sputter deposited at 310 °C from a Kr-plasma at a pressure of 0.1 Pa. The Kr-Si atom ratio was varied, resulting in a-Si:Kr with differing Kr concentrations. The Kr concentration was determined by Rutherford Backscattering (RBS).

2) a-Si grown by Plasma Enhanced Chemical Vapour Deposition (PECVD) at temperatures ranging from 50 °C to 200 °C and from a 2:1 mixture of SiH_4:H_2 (rf-power during deposition was 20 W at a frequency of 13.56 MHz).

---

[1] *Present address:* Département de Physique, Université de Montréal, Département de Physique, C.P. 6128, succ. "A", Montréal, Québec, H3C 3J7 Canada,

3) Ion beam amorphized silicon, prepared by implantation of 0.5 and 1 MeV Si^+-ions at −100 °C, resulting in a uniform 500 nm a-Si layer. The sample has been annealed at 500 °C, i.e. just below the recrystallization temperature. In a similar ***as-implanted*** sample an additional 50 keV H^+-implantation to a dose of 5×10^{16} cm^{-2} has been performed at room temperature. This sample was annealed in vacuum at 150 °C for 2, 6 and 25 hours respectively (see further [1]).

4) a-Si grown in a Molecular Beam Epitaxy (MBE) system. The first 10 nm was grown at room temperature, followed by 300 nm at 250 °C and a postgrowth anneal of 30 min. at 350 °C. Raman measurements show that at least 99 % of the overgrowth is amorphous.

Table 1. The fitted values of the S-parameters and the positron diffusion lengths of the Si-layers of the samples examined.

	scaled S	diff. length
monocrystalline Si		
c-Si	1.0000	245 nm
Kr-sputtered Si		
a-Si (0.55 % Kr)	1.0240	13.8 nm
a-Si (1.0 % Kr)	1.0244	12.6 nm
a-Si (2.7 % Kr)	1.0213	8.7 nm
a-Si (3.0 % Kr)	1.0209	7.0 nm
a-Si (3.9 % Kr)	1.0170	7.1 nm
a-Si (4.8 % Kr)	1.0183	8.0 nm
PECVD Si		
a-Si:H (50 °C)	1.0651	2.4 nm
a-Si:H (100 °C)	1.0534	2.4 nm
a-Si:H (150 °C)	1.0364	3.3 nm
a-Si:H (200 °C)	1.0273	6.2 nm
ion beam Si		
as-impl. a-Si (−100 °C)	1.0379	8.6 nm
annealed a-Si (500 °C)	1.0257	15.5 nm
ion beam a-Si + 50 keV H^+		
—	1.0391	6.5 nm
25 h anneal (150 °C)	1.0249	5.3 nm
MBE-system grown Si		
a-Si	1.1450	5.4 nm

All samples were examined with slow positrons, whereas the Kr-sputtered and 'MBE'-samples were also characterized with Raman-spectroscopy. Besides, the PECVD layers have been studied with Small Angle X-ray Scattering (SAXS) and the Ion beam samples by free carrier lifetime measurements.

The analysis of the data was done with the VEPFIT-program [2]. All S-values presented in this article, have been scaled to the fitted *c*-Si S-value and are therefore properly $S/S_{c\text{-Si}}$-values.

RESULTS AND DISCUSSION

The results of the measurements are shown in figs. 1–4 and the fit results are summarized in table 1.

The S-parameter of Kr-sputtered a-Si ranges linearly between 1.024 for low Kr-concentrations (0.5 and 1 %) to 1.018 for high concentrations (3–5 %). The positron diffusion length in the latter a-Si:Kr-layers is significantly lower than the one in a-Si with a low Kr-concentration.

Apparently, the 50 eV Kr creates Si self-interstitials which fill the grown-in vacancy-type defects, thereby reducing their size. On the other hand the electrically inactive Kr-atoms themselves fill the positron-traps. Both effects result in dense a-Si for a high Kr-concentration, corresponding to a lowering of the S-parameter. Nevertheless, the decrease of the diffusion length evidences more positron traps in the case of high Kr-concentrations. Though the Kr atoms and the Si self-interstitials have completely occupied the vacancies in the material, the oversized Kr atoms induce smaller positron traps due to the straining of the lattice.

This explanation is consistent with Raman-measurements, which show that the the *hwhm* of the Transverse Optical (TO) peak increases from 38.5 cm^{-1} for a-Si with

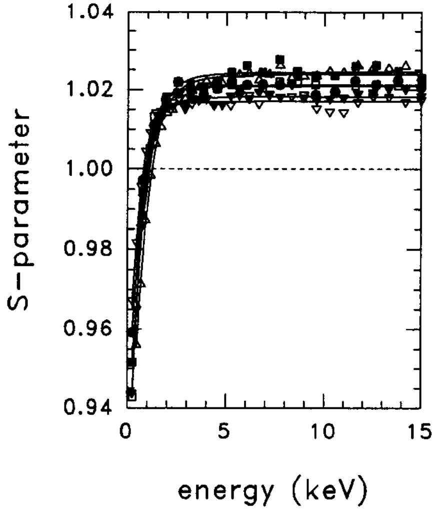

Figure 1. S-parameter *vs.* positron incident energy for Kr-sputtered a-Si containing 0.55 % (top curve) to 4.8 % Kr (lowest curve).

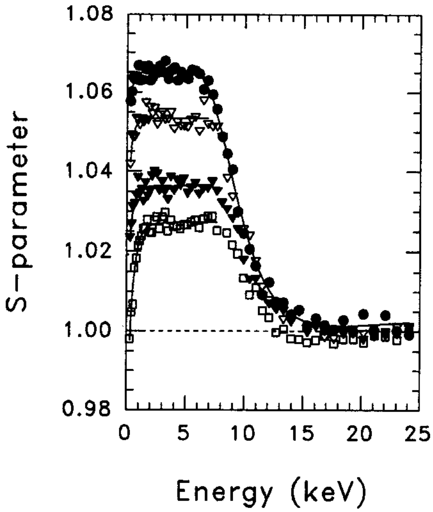

Figure 2. S-parameter *vs.* positron incident energy for PECVD a-Si grown at 50 °C (top curve), 100 °C, 150 °C and 200 °C (bottom curve).

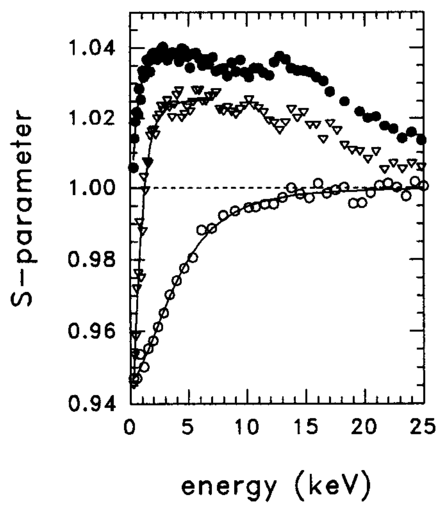

Figure 3. S-parameter *vs.* positron incident energy for c-Si (bottom) and *as-implanted* and *annealed* ion beam amorphized Si (top and middle curve).

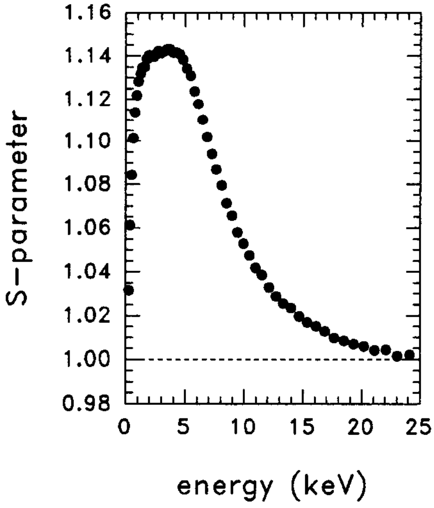

Figure 4. S-parameter *vs.* positron incident energy for MBE-system grown a-Si.

0.55 % Kr to 43.5 cm^{-1} for a-Si with 4.8 % Kr. Therefore, the mean bond angle distortion of a-Si is larger for a-Si with much Kr, corresponding to less ordering on the short range. As a reference: MBE a-Si has a TO_{hwhm} of 37.2 cm^{-1}, while it contains large voids. We conclude: More Kr in the lattice leads to a larger bond angle distortion, which corresponds to less short-range order and results in a shorter positron diffusion length [3].

The S-parameter of PECVD a-Si:H ranges between 1.027 for material grown at 200 °C and 1.065 for 50 °C a-Si. The diffusion length decreases for these samples from 2.4 nm to 6.2 nm.

The high S-parameter indicates Positronium (Ps) formation, at least in the 50 °C sample, showing the a-Si:H contains large voids. Positrons trapped in small open-volume defects in a-Si have S-parameters of about 1.035 [4]. Extremely high S-values can only be the result of zero-momentum annihilations of para-Ps in (large) voids, which has indeed been observed in PECVD a-Si:H via both 2D-ACAR and positron lifetime measurements [5–6]. The rather low S-parameter for the 150 °C and 200 °C a-Si, even lower than the S-parameter for vacancy-type defects mentioned above, can be explained by the presence of Si–H bonds in the small voids. These bonds change the electron momentum density in the neighbourhood of the trapped annihilating positrons, apparently leading to a lower S. This explanation is consistent with the much higher S-parameter found for MBE-system grown a-Si, where no hydrogen is present (see below).

Small Angle X-ray Diffraction (SAXS) measurements have shown that the free volume fraction of this a-Si increases from a few percent for the 200 °C growth up to 12 % for the poor-quality 50 °C growth [7]. This is in accordance with our measurements, which show that both the size of the voids ($\sim S$) and the number of the voids ($\sim$diffusion length) reduce for higher deposition temperatures.

The S-parameter of ion beam amorphized Si is 1.038 after the implantation, but decreases upon annealing (500 °C) to 1.026. The diffusion length increases from 8.6 to 15.5 nm. After H-implantation in the *as-implanted* a-Si the S-parameter remains at 1.039 and decreases only after prolonged heating at 150 °C. The diffusion length slightly decreases from 6.5 to 5.3 nm, although these values are not completely beyond doubt, because the diffusion length is obtained from positron measurements in the surface region of the a-Si where there should be no implanted H.

By the Si-implantation defects are introduced in the Si, which eventually leads to a complete amorphization. The resulting network of structural defects of the a-Si contains many dangling and/or strained bonds. Positrons are trapped in the vacancy-type defects present in the lattice. Upon thermal annealing the strained bonds relax, while the dangling-bonds can be passivated by hydrogen. In the former case the number of defects decreases in accordance with the increase of the positron diffusion length. From the decrease of S it can be concluded that the mean radius of the vacancy-type defects lowers by the anneal.

Assuming the divacancy trapping rate of c-Si (3×10^{14}, [8]) to be a typical positron trapping rate in damaged Si, we can estimate the concentration of positron traps. The trap-density in the *as-implanted* a-Si would correspond to 1.2 at.%, while the defect density in 500 °C annealed a-Si is found to be 0.4 at.% [1].

H-implantation and subsequent annealing at 150 °C also leads to a lowering of the S-parameter. This temperature is too low for any significant structural changes to occur.

It is well-known that H passivates dangling bonds, which according to photocarrier lifetime measurements has also taken place in the H-implanted and annealed sample [1]. This passivation can be related to the measured decrease in S, probably due to reduced trapping in the larger 'voids'. It appears, therefore, that some of the vacancy-type defects which were able to trap positrons no longer serve as those traps after the dangling bonds have been passivated with H. This means that at least some of the original dangling bonds were located at vacancy-type defects.

Finally, the S-parameter of MBE-system grown a-Si amounts to 1.145, which is really very large, but in accordance with the value of 1.15 for MBE grown Si with large voids [4]. The only adequate explanation of this value is para-Ps formation in large cavities. Simpson *et al.* found voids of 3 to 6 nm diameter [4]. The diffusion length of 5.4 nm is rather small, indicating poor-quality material, although it is not as small as in some of the PECVD a-Si:H-layers. Raman-measurements show a rather small bond-angle distortion (TO_{hwhm}=37.2 cm^{-1}).

In conclusion it has been shown that positrons are sensitive probes for a characterization of several types of a-Si. Changes in the S-parameter and diffusion length can be related to the presence of incorporated gases and voids or vacancy-type defects.

REFERENCES

[1] S. Roorda, R.A. Hakvoort, A. van Veen, P.A. Stolk and F.W. Saris, *submitted to J. Appl. Phys.*

[2] A. van Veen, H. Schut, J. de Vries, R.A. Hakvoort and M.R. IJpma, *in:* P.J. Schultz, et al.: *Slow Positron Beams for Solids and Surfaces*, Proc. 4th Int. Positron Workshop (AIP, New York, 1990), p.171.

[3] M.J.W. Greuter, L. Niesen, R.A. Hakvoort, J. de Roode, A. van Veen, A.J.M. Berntsen, W.G. Sloof, *to be published in:* Proc. 9^{th} Int. Conf. on Hyperfine Interactions, August 17-21, 1992, Osaka, Japan.

[4] P.J. Simpson et al., *in:* P.J. Schultz, et al.: *Slow Positron Beams for Solids and Surfaces*, Proc. 4th Int. Positron Workshop (AIP, New York, 1990), p.125.

[5] V.G. Bhide, R.O. Dusane, S.V. Rjarshi, A.D. Shaligram and S.K. David, J. Appl. Phys., **62**, 108 (1987)

[6] R. Suzuki, Y. Kobayashi, T. Mikado, A. Matsuda, P. McElheny, S. Mashima, H. Ohgaki, M. Chiwaki, T. Yamazaki and T. Tomimasu, Jpn. J. of Appl. Phys, **30**, 2438 (1991).

[7] M.J. van den Boogaard, S.J. Jones, Y. Chen, D.L. Williamson, R.A. Hakvoort, A. van Veen, A.C. van der Steege, W.M. Arnold Bik, W.G.J.H.M. van Sark and W.F. van der Weg, *to be published* (MRS Spring meeting 1992).

[8] M. Shimotomai, Y. Ohgino, H. Fukushima, Y. Nagayasu, T. Mihara, K. Inoue and M. Doyama, *in: Defects and Radiation Effects in Semiconductors*, Inst. Phys. Conf. Ser., **59** (Institute of Physics, London, 1981), p.241.