Materials Science Forum Vols. 105-110 (1992) pp. 1391-1394

POSITRON BEAM ANALYSIS OF AMORPHOUS SILICON

R.A. Hakvoort (a), S. Roorda (b), A. van Veen (a),
M.J. van den Boogaard (c), F.J.M. Buters and H. Schut (a)
(a) Interfaculty Reactor Inst. Delft University of Technology, Mekelweg 15, NL-2629 JB Delft, The Netherlands
(b) FOM Inst. for Atomic and Molecular Physics, Kruislaan 407,
NL-1098 SJ Amsterdam, The Netherland
present address: Univ. de Montréal, Département de Physique, C.P. 6128, succ. "A", Montréal, Québec, H3C 3J7, Canada
(c) Utrecht University, Debye Inst., Dept. of Atomic and Interface Physics, P.O. Box 80000, NL-3508 TA Utrecht, The Netherlands

Keywords: amorphous silicon, positron analysis, defects, hydrogenation, ion implantation, CVD, sputtering

ABSTRACT

S-parameter positron beam measurements have been done on CVD-grown, krypton sputtered and MeV Si ion beam amorphized silicon. The results obtained for ion beam a-Si can be interpreted as trapping in small vacancy-like defects which can be annealed. The presence of H in CVD a-Si or Kr in Kr-sputtered a-Si causes the diffusion lengths to be considerably larger than in a-Si without incorporated gas. Results obtained with implanted hydrogen in a-Si indicate passivation of dangling bonds by H.

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

Three types of a-Si have been examined:

1) a-Si grown by Chemical Vapour Deposition (CVD) at 100 °C from a 2:1 mixture of SiH_4:H_2 (rf-power during deposition was 20 W at a frequency of 13.56 MHz).

2) a-Si sputter deposited at 360 °C from a Kr-plasma at a pressure of 0.1 Pa. The Kr concentration in the layer was 6.6%, as determined by Rutherford Backscattering (RBS). As a reference polycrystalline Si (*poly*-Si) with a grain size of approximately 20 nm was grown at 580 °C, containing 0.2% Kr.

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. This 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]).

All samples were examined with slow positrons. The analysis of the data was done with the VEPFIT-program [2]. All S-values

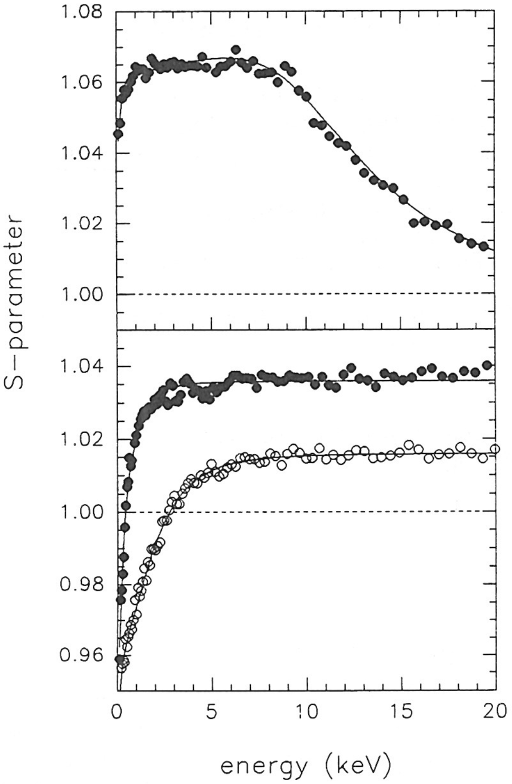

Figure 1. S-parameter versus positron incident energy for the CVD-grown a-Si layer (top) and for the two Kr-sputtered layers (bottom). In the latter plot the filled circles (●) represent the a-Si layer and the open circles (○) the *poly*-Si layer. The drawn lines are VEPFIT curve fits.

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

Figure 1 shows the results for the CVD-grown and the two Kr-sputtered Si-layers, figure 2 the results for the *as-implanted* and the annealed ion beam amorphized Si as well as for c-Si, and figure 3 shows the positron measurements of the H-implanted ion beam amorphized silicon sample after implantation and the successive annealing treatments. Table 1 contains a summary of the fitted values of the S-parameters and of the positron diffusion lengths in the Si-overlayers.

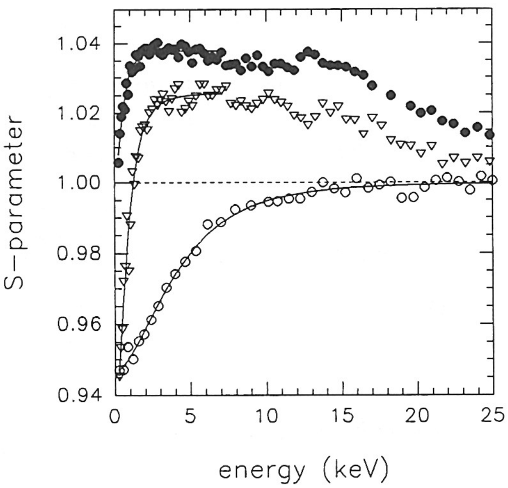

Figure 2. S-parameter versus positron incident energy for the ion beam amorphized silicon layers. The filled circles (●) represent the *as-implanted* a-Si, the open diamonds (▽) the annealed (500 °C) a-Si. The open circles (○) are the measured data of c-Si. The drawn lines are VEPFIT curve fits.

It appears that the S-parameters and diffusion lengths in a-Si depend strongly on the way in which the layers are prepared. Previous S-parameter measurements of bulk a-Si by several authors have shown similar results. There is general agreement that the S-value of a-Si is higher than the one of c-Si, but the deposition method may influence the precise value greatly [3,4,5].

Our measurements yield (scaled) S values of a-Si between 1.0255 for the annealed ion beam a-Si and 1.0680 for the CVD a-Si. In between lie the values for *as-implanted* ion beam a-Si (1.0377) and Kr-sputtered a-Si (1.0324). Kr-sputtered *poly*-Si has the lowest S-value (1.0255) apart from c-Si (1.0000).

There is an obvious difference between the several types of a-Si. The high S-value of the CVD a-Si can be accounted for by the presence of large voids, possibly causing positronium formation. CVD a-Si contains much built-in hydrogen (about 10%), but the H^+-implantation into initially hydrogen free a-Si

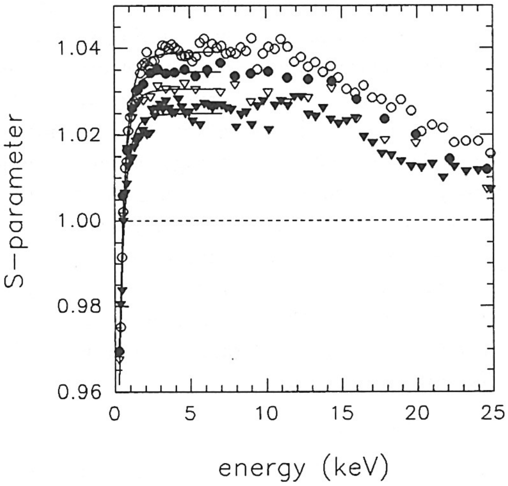

Figure 3. S-parameter versus positron incident energy for the H-implanted (50 keV) ion beam amorphized Si. The open circles (○) represent the data of the *as-implanted* ion beam a-Si, the filled circles (●), open diamonds (▽) and filled diamonds (▼) the measurements of the same sample after annealing at 150 °C for 2, 6 and 25 hours respectively. The drawn lines are VEPFIT curve fits.

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
CVD Si		
a-Si:H (100 °C)	1.0680	12 nm
Kr-sputtered Si		
a-Si (360 °C)	1.0324	19 nm
poly-Si (580 °C)	1.0125	58 nm
ion beam Si		
as-impl. a-Si (−100 °C)	1.0377	8 nm
annealed a-Si (500 °C)	1.0255	16 nm
ion beam a-Si + 50 keV H^+		
—	1.0391	7 nm
2 h anneal (150 °C)	1.0344	5 nm
6 h anneal (150 °C)	1.0308	5 nm
25 h anneal (150 °C)	1.0249	5 nm

does not lead to a high S-parameter (figure 3). Though Kr-sputtered a-Si contains a considerable amount of incorporated gas (like the CVD a-Si), the material is more like ion beam a-Si. There are some indications that Kr-vacancy complexes are probably not a very effective positron trap, the Kr apparently prohibiting the positron from trapping in the vacancy. Actually, ion beam amorphized Si is a-Si with the highest density (there are neither voids nor gas atoms present), but the S-parameter of the *as-implanted* sample is not the lowest one. Note, however, the difference in the preparation temperature for the two samples, which might account for this discrepancy. Only after the 500 °C anneal the S-value decreases below the one for Kr-sputtered a-Si.

The positron diffusion lengths of the various samples differ too. Positrons in c-Si have a diffusion length of 245 nm. The diffusion length in the Kr-sputtered *poly*-Si is 58 nm and all diffusion lengths in the a-Si samples are shorter. Of these amorphous layers Kr-sputtered a-Si has the longest diffusion length (19 nm), another indication of reduced positron trapping at vacancies occupied by Kr atoms. CVD a-Si has one of 12 nm and the ion beam amorphized Si one of 8 nm. This last value doubled to 16 nm as a result of the 500 °C anneal. All values of the diffusion length in a-Si are unusually long for amorphous solids, which do not contain any long range order and may as a result have relatively high concentrations of positron traps. Therefore, we must assume that most of these traps in a-Si are shallow, so that positron diffusion consists of hopping from one trap to another.

The annealing of the ion beam amorphized Si makes clear that even in a-Si 'defects' are present which can be removed by annealing. Note that the anneal temperature (500 °C) lies well below the recrystalization temperature of Si (550 °C), the annealed layer therefore being amorphous too. The difference between the two is not one of short range ordering, but of (structural) strain relaxation. Differential Scanning Calorimetry (DSC) measurements show a heat release of about one third of the heat of crystallization at low temperatures (i.e. below 550 °C) [1]. This relaxation can be viewed as the annealing of defects from the a-Si layer, which form rather deep traps. Assuming a specific trapping rate for divacancies of 3×10^{14} s^{-1} the *as-deposited* ion beam amorphized Si corresponds to c-Si with 1.5 at.% divacancies and the annealed a-Si to c-Si with 0.3 at.% divacancies. Therefore, ion beam amorphized Si might be viewed as a-Si in which trapping occurs only at deep traps, present in a concentration of a few percent, in quantitative accordance with both DSC and Raman measurements [1].

The 50 keV H^+ implantation in the *as-implanted* ion beam amorphized Si did not have any measurable effect. Both the S-parameter and the diffusion length remained the same. After annealing at 150 °C the S-parameter went down. This reduction of S was absent at an anneal of *as-implanted* ion beam a-Si at 150 °C (not shown). On the other hand the diffusion length did not increase, but even decreased slightly. This latter effect may be accounted for by the fitting program which derives the diffusion length from the data at low energies (first few keV), where no H is present. However, in the plots in figure 3 there is no implantation profile visible, which should be there due to the localization of the implanted hydrogen. The projected range of 50 keV H in Si amounts to 500 nm with a straggling of 100 nm [6], while hydrogen is only limited mobile in a-Si at a temperature of 150 °C [7].

We tend to explain the data in the following way. Ion beam amorphized Si has about 10^{19} dangling bonds (DB's) per cm^{-3} [7], i.e. a concentration of 2×10^{-4}. Usually DB's are related to vacancy-type defects and may act thus as positron traps. Especially negatively charged vacancies may cause enhanced trapping [8]. The estimated defect concentration of 3% for *as-implanted* a-Si is much higher than the concentration DB's, so we conclude that part of the trapping is at electrically neutral vacancy-type defects. After H implantation and the successive anneal H-atoms bind to the dangling bonds resulting in reduced positron trapping, thereby resembling CVD a-Si which contains only 10^{15}–10^{16} DB's per cm^{-3} [7]. The H concentration after the implantation amounts (locally) to 5%, which should be high enough for the passivation of most of the DB's. However, the absence of a profile in figure 3 is not yet satisfactorily explained.

CONCLUSION

Various types of a-Si can be studied and even distinguished with slow positron beam analysis. The measured S-parameters and positron diffusion lengths depend strongly on the way in which the layers are prepared. Annealing of *as-implanted* ion beam amorphized Si results in a-Si with different annihilation characteristics. Positron annihilation is able to distinguish between this unrelaxed and relaxed a-Si.

ACKNOWLEDGEMENT

Work at FOM was financially supported by the Nederlandse Organisatie voor Wetenschappelijk Onderzoek (NWO) and the Stichting Technische Wetenschappen (STW).

REFERENCES

1) Roorda, S., et al.: Phys. Rev. B, **44**, *in press.*

2) Veen, A. van, et al.: *in:* P.J. Schultz, et al.: *Slow Positron Beams for Solids and Surfaces*, Proc. 4th Int. Positron Workshop, American Institute of Physics, New York, 1990, 171.

3) Leo, P.H., et al.: *Phys. Stat. Sol. B*, 1981, **108**, K145.

4) Jung, A.L., et al.: *J. Non-cryst. Solids*, 1985, **77–78**, 221.

5) Xiong, J.J., et al.: *in:* P.C. Jain, et al.: *Positron Annihilation*, Proc. ICPA-7, World Scientific, Singapore, 1985, 744.

6) Andersen, H.H., e.a.: *Hydrogen, Stopping Power and Range in all Elements*, Pergamon, New York, 1977.

7) Kakalios, J., *in:* J.I. Pankove, et al.: *Hydrogen in Semiconductors*, Academic Press, Boston, 1991, 381.

8) Puska, M.J., et al.: *Phys. Rev. B*, 1990, **41**, 9980.