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CHARACTERIZATION OF SILICON IMPLANTED SiO_2 LAYERS USING POSITRON ANNIHILATION SPECTROSCOPY

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Abstract

Silicon implanted thermal SiO_2 layers were studied using depth-resolved positron annihilation spectroscopy (PAS) and transmission electron microscopy (TEM). TEM observations show the presence of silicon nanocrystals (Si_{nc}) in the region between 200 nm and 300 nm. The defect annealing behavior is studied by means of PAS. For 1000 ^oC annealed samples at a depth for which Si_{nc} are observed, a distinctive PAS signal is detected and ascribed to the Si_{nc}/SiO_2 interface.

INTRODUCTION

Visible light emission from silicon based nanostructures has attracted interest in the last years since the observation of luminescence from porous silicon [1]. Although many theoretical and experimental studies have been conducted, the physical process responsible for the emission is not perfectly clear. Quantum confinement within Si_{nc} [1,2,3], emission from molecular species such as siloxene [4] and recombination near the Si/SiO_2 interface [5,6], have been proposed as light emission mechanisms. Recently on silicon implanted thermal SiO_2 layers visible light emission showing similarities with that of porous silicon was observed [7,8,9]. This emission, which was observed only after 1000 ^oC annealing, was related to Si_{nc} which are formed after thermal annealing [7,8] or to defects at the Si_{nc} / SiO_2 interface [9].

DISCLAIMER

were annealed *in situ* by a resistively heated tantalum foil and the temperature was monitored by a thermocouple. Above 700 °C annealings were performed in N_2 atmosphere.

RESULTS AND DISCUSSION

Positron S-parameter depth profiles for an unimplanted layer, for a sample implanted at $2x10^{17}cm^{-2}$ dose, and after subsequent annealing at 700 °C and 1000 °C, are reported in Fig. 1.

For a given energy, the implantation profile can be approximated by a Makhovian distribution and the mean implantation depth is related to energy by the relation :

$$z = A / \rho E^n \qquad (1)$$

where A = 4.0 μg cm^{-2} keV^{-n}, n = 1.6, and ρ is the material density. Positrons, after being thermalized, annihilate within a spatial range which is of the order of the diffusion length (10 nm for SiO_2).

Fig .1 shows that in the region corresponding to the SiO_2 layer the S-parameter decreases after implantation. The reduction cannot be caused by the creation of bigger open-volume defects. Inside open-volume defects positrons encounter low-momentum valence electrons with higher probability. This give rise to a narrowing of the annihilation-line and therefore to a higher S-parameter.

To understand the origin of the defects produced during ion implantation thermal annealing was performed up to 1000 °C in steps of 100 °C. The results reported in fig. 2 show that the recovery of the oxide S value starts around 300 °C. The unimplanted value is restored around 700 °C.

Defects that are possible candidates for giving a low S-parameter in bulk SiO_2 are the so-called non-bridging-oxygen hole-centers (NBOHC) but they usually anneal below 300 °C [13]. Similar annealing behavior was observed in SiO_2 layers implanted with B by Fujinami and Chilton [14], and in SiO_2 layers implanted with Si by Nielsen et al. [15], but in both cases this defect center was not identified.

Most of the changes in the S vs. energy curve occur at shallow depths (between surface and 200 nm) for annealing below 1000 °C. After 1000 °C annealing the S-parameter decreases in the region between 200 nm and 400 nm (see Fig. 1). For 1000 °C annealed sample, the S-value around 600 nm is significantly lower than that of the unimplanted sample. A visual inspection of the slope of the S-energy curve from 400 nm to 2000 nm, shows an increase in positron diffusion length in silicon. Therefore the low S-parameter is related to the increased fraction of positrons implanted in silicon, diffusing back to the implanted layer and annihilating there.

To study the origin of the low S value in the region corresponding to the mean Si implantation depth, samples implanted at different doses were studied. Fig. 3 shows S vs. energy spectra for samples implanted in the dose range of $3x10^{16}$ cm^{-2} - $3x10^{17}$ cm^{-2} and subsequently annealed at 1000 °C. As shown in Fig.1, the near-surface layer recovers after 1000 °C anneal. The behavior observed for all the samples can be described assuming that only the region between 100 nm and 400 nm, i.e. the Si implanted region, is changing. The decrease in the S value depends on Si dose and it is increasing for increasing implantation dose. Fig.4 shows TEM picture for sample implanted at $3x10^{17}$ cm^{-2} dose and annealed at 1000 °C. Silicon nanocrystals are visible in the region between 200 nm and 300 nm. These facts suggest that the observed low S-parameter is related to n-Si which are formed during 1000 °C annealing.

Low S-parameter can be detected in bulk SiO2 when positrons annihilate at NBOHC but these defects anneal below 300 °C as already remarked. Positrons annihilating with oxygen core electrons can give a low S-value. Defects like O^+ centers, altough they may exist, cannot trap positrons since they are positively charged.

For the Si/SiO_2 system a S value lower than that of Si and SiO_2 was observed [11] and related to positron trapped and annihilating at the interface. Au et al. [15] proposed a model in which positrons are trapped at the interface and anneal with oxygen core electrons giving rise to a broadening in the annihilation line and to a low S value.

Considering this anology and the fact that the S-parameter reduction is higher in samples implanted at the highest dose, we suggest that the signal responsible for the low S value can be ascribed to positron annihilating at the interface between the silicon nanocrystals and the host SiO_2. A clear minimum in the S vs. energy curves with increasing dose, appears around 230 nm, consistent with the formation of a Si/SiO_2 interface. Although the S value in the region in which

Si_{nc} precipitates are observed exhibits an interface-like behavior, this region can have properties different from the SiO_2/bulk Si interface.

These preliminary results show that PAS has a high sensitivity to the Si_{nc}/SiO_2 interface. PAS studies of the Si_{nc}/SiO_2 region under different conditions (hydrogen annealing, bias voltage applied across the oxide layer) can provide informations about the properties of this transition region, similarly to what was already performed on the SiO_2/ bulk Si interface ([17,18]). A better understanding of the nature of the Si_{nc}/SiO_2 interface can be useful, if coupled with optical techniques (continous and time-resolved photoluminescence), to clarify the role played by this interface in the light emission process.

CONCLUSIONS.

Positron annihilation spectroscopy and transmission electron microscopy experiments were conducted on Si implanted SiO_2 layers. Based on the annealing behavior, the low S value observed only after 1000 °C annealing in the region where Si_{nc} were observed, was related to Si_{nc} formation. It is discussed that the low S value can be associated with positrons annihilating at the Si_{nc}/SiO_2 interface.

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REFERENCES

[1] L. T. Canham, Appl. Phys. Lett. **57**, 1046 (1990)

[2] V. Lehmann and U. Gosele, Appl. Phys. Lett **58** 856 (1991)

[3] B. Delley and E.F. Steigmeier, Phys. Rev. B **47**, 1397 (1993)

[4] M.S. Brandt, H.D. Fuchs, M. Stutzmann, J. Weber and M. Cardona, Solid State Comm. **81**, 307 (1991)

[5] F. Koch, Mat. Res. Soc. Symp. Proc. **298**, 319 (1993)

[6] S.M. Prokes and O.J.Glembocki, Phys. Rev. B **49**, 2238 (1994)

[7] P. Mutti, G. Ghislotti, S. Bertoni, L. Bonoldi, G.F. Cerofolini, L. Meda, E. Grilli and M. Guzzi, Appl. Phys. Lett **66**, 851 (1995)

[8] T. Komoda, J. Kelly, F. Cristiano, A. Neijm, P.L.F. Hemment, K.P. Homewood, R.Gwilliam, J.E. Mynard, B.J. Sealy, Nuc. Instr. and Methods B **96**, 387 (1995)

[9] T. Shimizu-Iwayama, K. Fujita, S.Nakao, K.Saitoh, T. Fujita, N. Itoh, J. Appl. Phys. **75**, 7779 (1994)

[10] P. Asoka-Kumar, K.G. Lynn and D.O. Welch, J. Appl. Phys. **76**, 4935 (1994)

[11] B. Nielsen, K.G. Lynn, Y.C. Chen and D.O. Welch, Appl. Phys. Lett **51**, 1022 (1987)

[12] P.J. Schultz and K.G. Lynn, Rev. Mod. Phys. **60**, 701 (1988)

[13] E.H. Poindexter, P.J. Caplan, and G.J. Gerardi, in *The Physics and Chemistry of SiO2 and the Si-SiO2 interface*, edited by C.R. Helms and B.E. Deal (Plenum, New York, 1988), p.304

[14] M. Fujinami and N.B. Chilton, Appl. Phys. Lett. **61**, 1131 (1993)

[15] B. Nielsen et al. , unpublished

[16] H.L. Au, P. Asoka-Kumar, C.D. Beling, S. Fung and K.G. Lynn, Phys. Status Solidi B **178**, K11 (1993)

[17] R. Khatri, P. Asoka-Kumar, B. Nielsen, L.O. Roellig, and K.G. Lynn, Appl. Phys. Lett **65**, 330 (1994)

[18] T. C. Leung, Z.A. Weinberg, P. Asoka-Kumar, B. Nielsen, G.W. Rubloff, and K.G. Lynn J. Appl. Phys. **71**, 530 (1992)

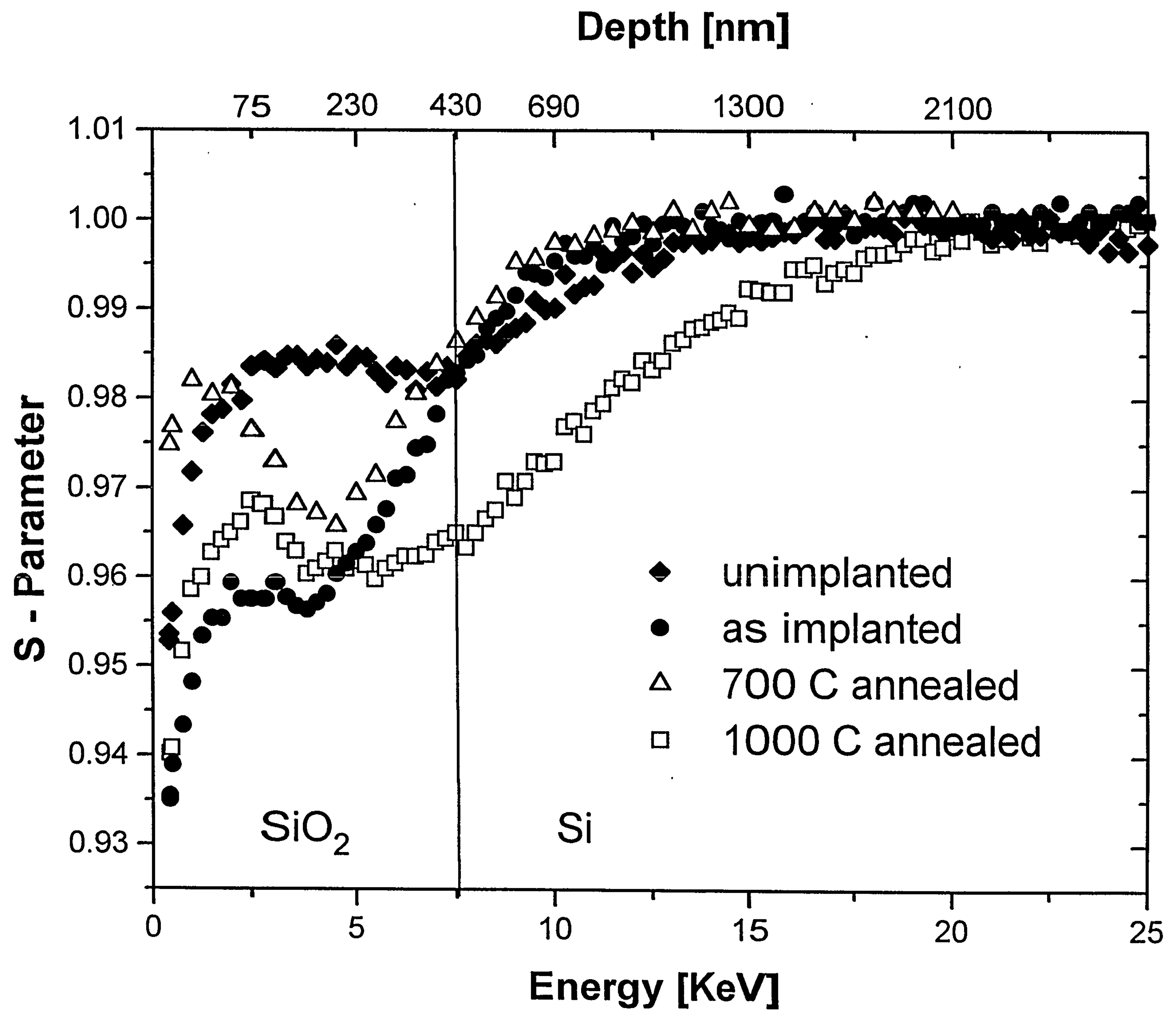
FIGURE CAPTIONS

Figure 1. S-parameter as a function of the positron implantation energy and mean implantation depth for unimplanted SiO_2 layer on Si and for sample implanted at 2 X 10^{17} cm^{-2}. Results after 700 °C and 1000 °C annealing are also shown.

Figure 2. S-parameter as a function of the annealing temperature for a positron energy corresponding to a mean implantation depth of 75 nm. The arrow represents the oxide S value before implantation.

Figure 3. S versus energy depence for samples implanted at different doses and annealed at 1000 °C. A monotonic decrease in the S-parameter when the dose is increased was observed.

Figure 4. TEM micrograph of a cross section of the $3x10^{17}$ cm^{-2} implant after 1000 °C annealing. Nanocrystals (bright spots) inside the SiO_2 matrix are visible. Inset: electron diffraction pattern. {200}, {111}, {220} and {113} electron diffraction rings are observed.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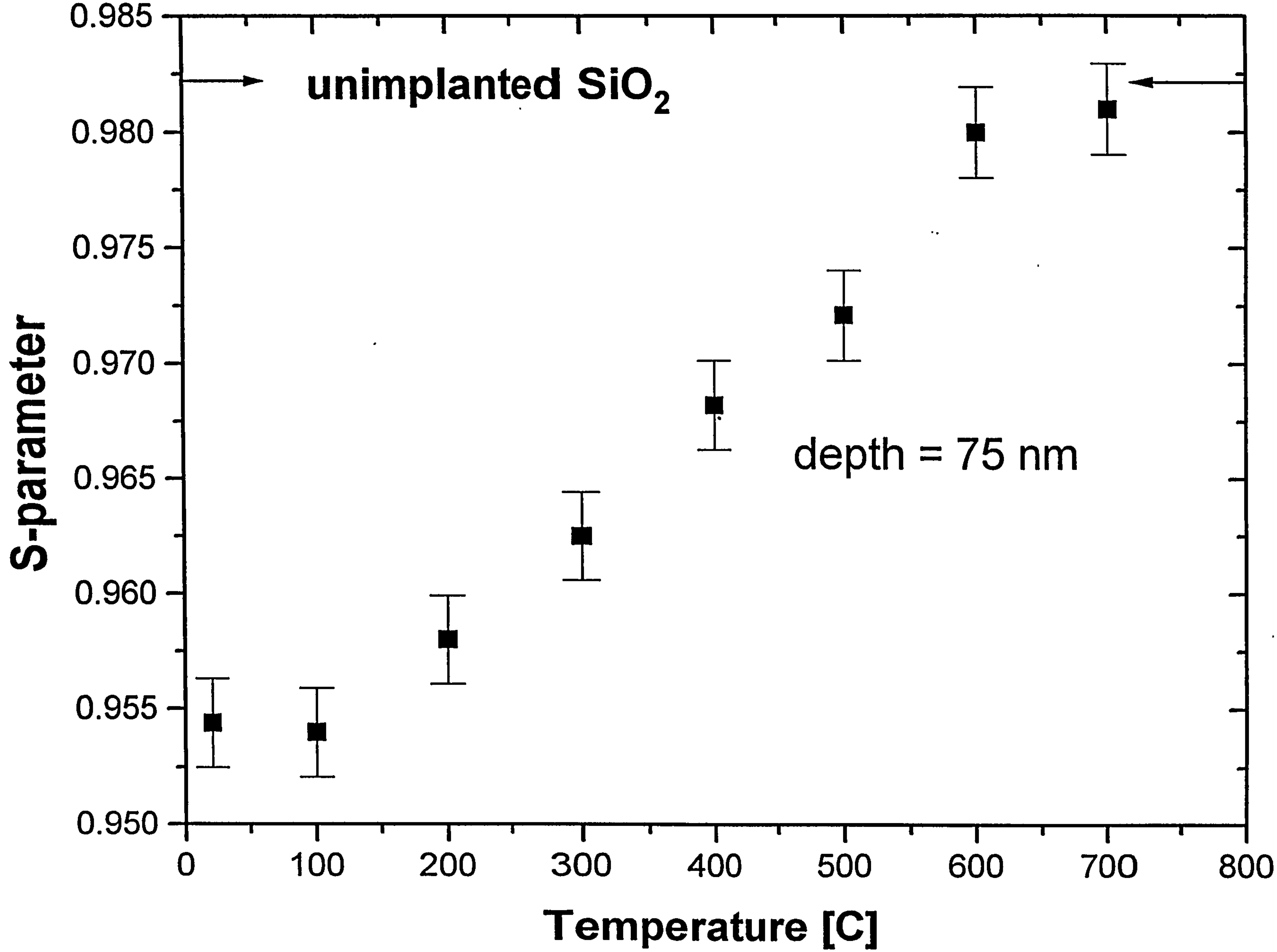
75
230
430
690
1300
2100
S - Parameter
1.01
1.00
0.99
0.98
0.97
0.96
0.95
0.94
0.93
unimplanted
as implanted
700 C annealed
1000 C annealed
SiO$_2$
Si
0
5
10
15
20
25
Energy [KeV]



unimplanted SiO2
depth = 75 nm
S-parameter
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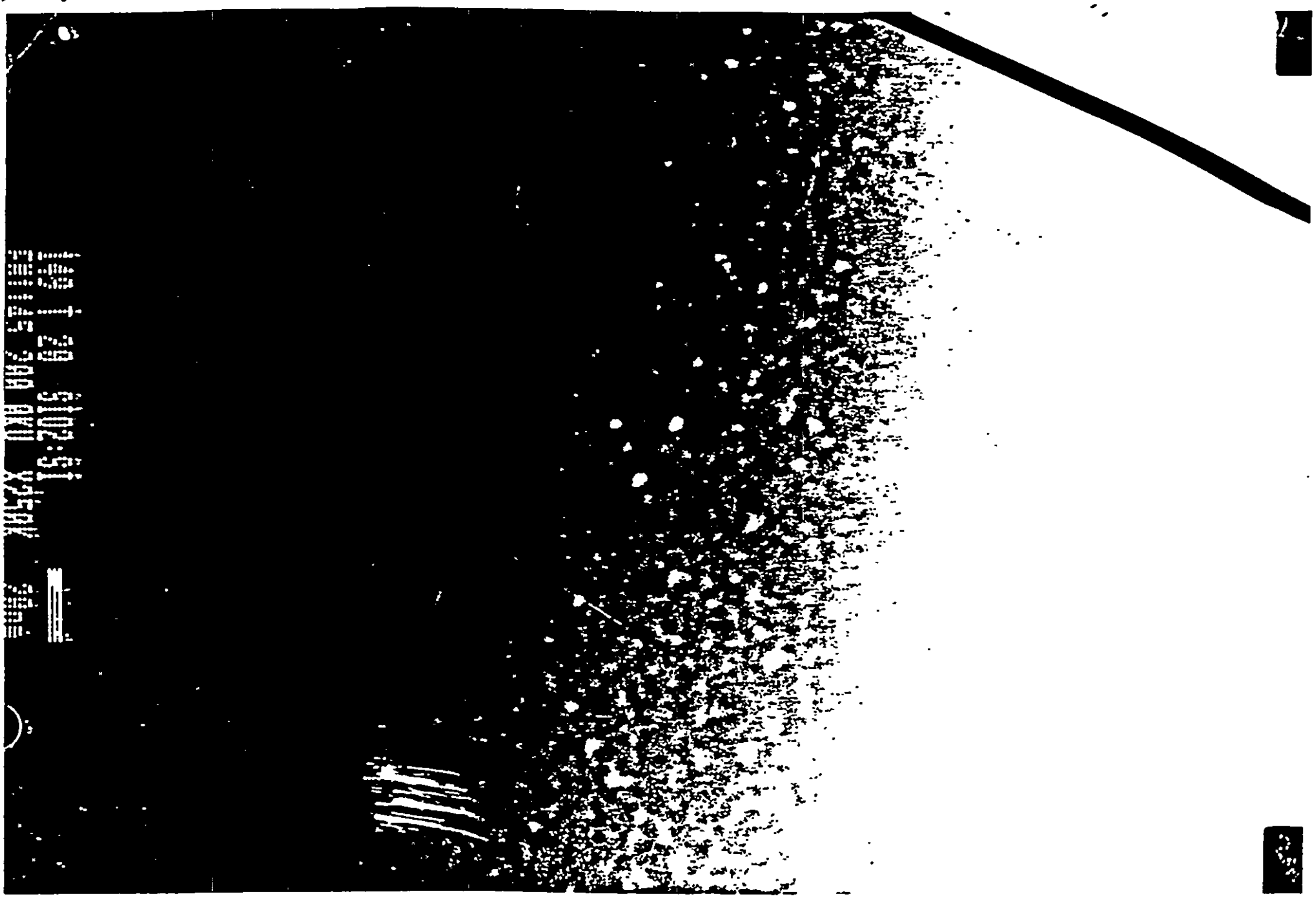
0.980
0.975
0.970
0.965
0.960
0.955
0.950
0
100
200
300
400
500
600
700
800
Temperature [C]



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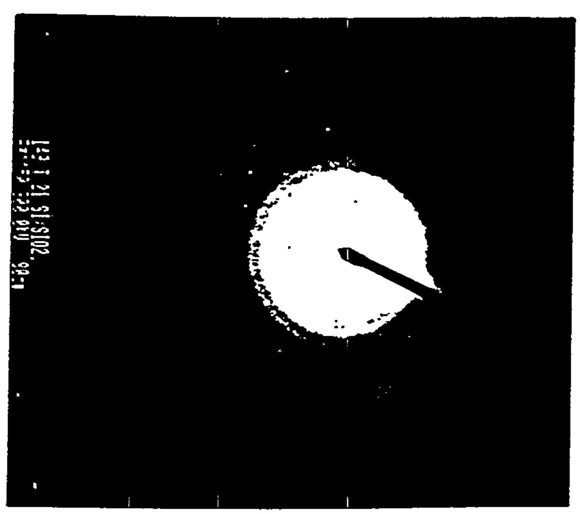

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