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ABSTRACT

High purity silica (Spectrosil) samples were implanted with Cu at doses from 0.5 x 10^{16} to 6.0 x 10^{16} ions/cm^2. Samples implanted to a dose of 6.0 x 10^{16} ions/cm^2 were implanted at dose rates of 7.5, 5, 2.6, and 0.7 μA/cm^2. Some samples were implanted with smaller total doses at dose rates of 7.5 and 2.5 μA/cm^2. Backscattering measurements determined the concentration of implanted ions as a function of dose and depth.

The optical absorption, measured from 1.8 to 6.0 eV at room temperature, was observed to increase with increasing dose rate in samples implanted with a total dose $\geq$ 3.0 x 10^{16} ions/cm^2. We attribute the increase in optical absorption at energies between 2 and 5 eV with dose in these samples to the formation of spherical copper colloids of various diameters. The peak at 2.2 eV that forms at dose levels $\geq$ 3.0 x 10^{16} was observed to increase nonlinearly with dose rate. We attribute this peak to the formation of prolate copper spheroids with an aspect ratio of ~2. We suggest that the dose rate dependence is due to localized heating which increases with increased dose rate.

Samples implanted with doses (3 x 10^{16} ions/cm^2 did not display this same strong dependence on dose rate. For these doses copper colloids are not a major source of absorption in the 2 to 5 eV range. In these samples we attribute the absorption to Cu^+ and to intrinsic defects produced by radiation damage.

INTRODUCTION

Interest in optical devices has lead to research on potential nonlinear optical materials.[1,2] Materials that have shown large nonlinearities are dielectrics embedded with metallic colloids.[3,4,5] Haus, et al.,[5] have suggested that appropriately shaped metallic colloids could lead to enhancements of $\chi^{(3)}$, the third order susceptibility on the order of 10^8, hence, leading to large values of n_2, the nonlinear index of refraction. The enhancements of $\chi^{(3)}$ are due to large local fields at the surface plasmon resonance frequency.[4,5] These enhancements may make possible all optical bistable switching devices as well as waveguide devices.[4,5,6]

Enhancements of $\chi^{(3)}$ have been observed with nanoclusters of gold and silver particles in water[3,6] and with gold particles in Schott filter glass (RG6)[5] at the surface plasmon resonance frequency of the metallic particles.

These same plasmon resonances result in the absorption and scattering of light and are the source of color in conventionally melted glasses containing metallic colloids. Thermal annealing to change the size of these colloids has been used for decades to control the color of the glasses. Bamford[7] and Rawson[8] have reviewed the literature on the formation of metallic colloids and the effects of annealing on the size of the colloids. Changes of the size, shape and numbers of particles of these colloids change both the linear and nonlinear optical properties.[5,7,8]

The formation of metallic colloids by ion implantation offers the possibility of creating new materials that are not attainable by conventional glass melting techniques. This new way of controlling colloid morphology is compatible with present optical waveguide formation and semiconductor technology.

Silver colloid formation has been reported by Arnold and Borders[9] with ion implantation in lithium silicate glasses. Perez, et al.,[10] reported the formation of Fe colloids in silica using ion implantation techniques. Magruder, et al.,[11] have reported the formation of metallic Cu colloids in high purity silica using ion implantation. They observed that the formation of colloids was dose and substrate temperature dependent.

As the usefulness of metallic colloids in glasses will, in large part, depend upon increasing $\chi^{(3)}$ through the control of the shape and size of the colloids, one purpose of this research was to investigate the effects of dose rate on the process of formation of copper colloids by ion implantation.

EXPERIMENTAL PROCEDURE

High purity silica (Spectrosil A)* substrates 2.0 cm in diameter and 0.1 cm thick were implanted with nominal doses ranging from 0.5 x 10^{16} to 6.0 x 10^{16} ions/cm^2 and with dose rates ranging from 7.5 μA/cm^2 to 0.7 μA/cm^2 at an ion energy of 160 KeV. Substrates were implanted at room temperature. Sample preparation has been previously reported.[12] Table I shows the nominal implantation dose and dose rate for all samples used. Ion backscattering techniques with 2 MeV He^+ ions were used to measure ion concentration as a function of depth from the implanted surface and have been described. The implantation and backscattering measurements were carried out at Oak Ridge National Laboratory. Optical measurements were made at room temperature in air from 650 nm to 200 nm (1.8 to 6.2 eV) using a Cary 14 dual beam spectrometer interfaced with a data acquisition system. All samples were measured using an unimplanted Spectrosil A sample in the reference beam. Differences in the thickness of implanted samples and the reference sample were ≤ 1%. Hence, all absorption measurements shown are the difference between implanted and unimplanted glasses. The spectra are shown as a function of absorption per implanted ion, i.e. extinction coefficient (EC).

The absorption spectra were measured at five different positions on each sample. The scatter in extinction coefficient for the five different positions was always greater than the uncertainty in intensity at one position. The scatter in extinction coefficient due to these five different positions is less than ±5%.

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*Source of samples was Thermal American Fused Quartz.

RESULTS

Table I gives the nominal number of implanted ions per cm^2 and the dose rate used. Nominal dose is the integrated current incident on a sample divided by the sample area. Rutherford backscattering measurements were made on all samples. Figure 1 shows the RBS data for doses of 1.0×10^{16} ions/cm^2 at 2.5 $\mu A/cm^2$, 3.0×10^{16} ions/cm^2 at 2.5 and 7.5$\mu A/cm^2$, and 6.0×10^{16} ions/cm^2 at .7 and 7.5 $\mu A/cm^2$. The concentrations as a function of depth are similar in shape for other doses. For a nominal dose of 1×10^{16} ions/cm^2, the distribution is Gaussian; whereas, for doses $\geq 3.0 \times 10^{16}$ ions/cm^2, the distribution is bimodal. This bimodal distribution is discussed elsewhere.[12] For samples implanted with the same nominal dose, the ion concentration profile, within error, was the same for different dose rates.

Figure 2 shows the EC as a function of energy from 1.8 to 6.0 eV for the samples with a nominal dose of 6.0×10^{16} ions/cm^2. The EC has a peak at 2.2 eV that increases monotonically with dose rate as does the EC at ~3 eV. The EC between 3.8 and 5.5 eV does not increase monotonically with dose rate. The absorption at 6.0 eV also increases monotonically with dose rate. Only the peak at 2.2 eV is clearly resolved. As seen in Figure 3 for the samples implanted with a nominal dose of 3×10^{16} ions/cm^2, the increase in EC with an increase in dose rate is approximately the same between 2.2 and 5.7 eV and at energies > 5.7 eV. The EC of samples implanted with a nominal dose of 1.0×10^{16} ions/cm^2 are, within experimental error, the same for both 7.5 and 2.5 $\mu A/cm^2$ dose rates as seen in Figure 4.

DISCUSSION

From the RBS data in Figure 1, the dose rate does not have an effect on the bimodal distribution observed for doses $\geq 3.0 \times 10^{16}$ ions/cm^2. However, the dose rate does affect the optical absorption for doses $\geq 3.0 \times 10^{16}$ ions/cm^2 as seen in Figures 2 and 3. For samples implanted with doses $\geq 3.0 \times 10^{16}$ ions/cm^2, we attribute the optical absorption in our samples from 3.8 to 4.8 eV to the formation of spheroidal Cu colloids with varying diameters and the

absorption peak at 2.2 eV to prolate (or oblate) copper spheroids with an aspect ratio of ~2. The basis for this attribution is that the free energy of formation[13] of CuO (-61.7 Kcal/mole) and Cu_2O (-35.5 Kcal/mole) is less than that for a-SiO_2 (-189.9 Kcal/mole); hence, the free energy of the Cu:Si is minimized by the formation of colloidal copper in samples with total dose $\geq 3.0 \times 10^{16}$ ions/cm^2. The peak absorption due to a spherical metal colloid in an insulator is given by Townsend[14] as

$$\lambda_m = \frac{2\pi c}{\omega} (1 + 2n_o^2)^{\frac{1}{2}}$$

where λ_m is the wavelength of the peak, c is the speed of light, n_o is the refractive index of the insulator and ω is the plasmon frequency of the colloid. We calculate λ_m using this formalism to be 4.8 eV. This peak wavelength is expected to shift to longer wavelengths with increasing particle size.[9,14] This shift has been observed for Ag colloids implanted in silicates.[9] Magruder, et al.,[11] have observed, in Cu implanted silica, an absorption between 3.0 to 4.8 eV and have attributed it to the formation of Cu colloids with varying diameters. The increasing absorption with increasing dose in the broad shoulder region from 2.8 to 4.0 eV they attribute to an increase in colloid diameters with increasing dose. As the colloids grow in size, there is a shift of λ_m to longer wavelengths. A range of sizes and small deviations from sphericity of such colloid particles will produce a large width to this absorption. The 2.2 eV peak we attribute to the formation of prolate copper spheroids with an aspect ratio of ~2. This assignment is based on the analysis of Magruder, et al.[11]

In our samples, the absorption at 3.0 eV increases with increasing dose rate as seen in Figures 1 and 2 for constant nominal dose. We attribute this increase to increases in numbers and sizes of the colloids. With an increase in dose rate, the energy deposited per unit time into the silica structure increases, increasing the local temperature. For a dose rate of 7.5 μA/cm^2 and an implantation energy of 160 KeV, there is 1.2 watt/cm^2 to be dissipated in the sample. As the

energy is being dissipated in a very small volume, ~0.2 x 10^{-4} cm thick, and the silica substrate is a good thermal insulator, we anticipate a large local heating effect. There is an order of magnitude difference for the power dissipated for the samples implanted at 7.5 $\mu A/cm^2$ and 0.7 $\mu A/cm^2$ (highest and lowest dose rate). Hence, we estimate an order of magnitude difference in the heat to be dissipated between highest and lowest dose rate.

Colloid formation will depend upon the nucleation rate of colloids, and their size will depend on diffusion rates of the metallic ions through the substrate material to the colloid sites.[15] The nucleation rate will depend upon the free energy of formation of the colloidal particles and diffusivity of the Cu ions. Thus we expect this rate of colloid formation to increase with increasing temperature, the exact temperature dependence of which is unknown. We expect the growth in the size of the colloids to be diffusion controlled. Hence, we attribute the increasing absorption at 3.0 to 4.1 eV with increasing dose rate to increase in sizes of particles. The local heating results in greater diffusivity of the Cu ions allowing for growth of the particles and the subsequent red shift of λ_m. Additional support for this argument comes from the suggestion by Magruder, et al.,[11] that the increase in absorption in this region with increasing substrate temperature during implantation is due to an increase in diffusivity.

The peak at 2.2 eV has the largest percentage increase in extinction coefficient with increasing dose rate. As this peak is attributed to small colloids with an aspect ratio of ~2, we suggest that this large increase is due to the enhanced growth and nucleation of this particular particle shape with increasing dose rate. We cannot, at this time, give an explanation for the formation of particles with an aspect ratio ~2.

For the samples implanted with a nominal dose of < 3 x 10^{16} ions/cm^2, we attribute the absorption for energies ≥ 5.0 eV to defects induced by the implantation process. Two defects with known optical absorption in this region are the B_2 (5.0eV) center and the E' (5.8 eV) center.[16,17] Both of these centers are oxygen vacancy centers created by the implanted ions displacing oxygen ions from their usual bonding sites in the glass. This oxygen can move off and form peroxy

linkages. A review of these centers, their formation and optical absorption, is given in references 16 and 17.

At dose levels $\leq 1 \times 10^{16}$ ions/cm^2, colloid formation is not observed (Fig. 4). We observe only a small absorption in the spectra at energies < 5.0 eV. As colloid formation is not observed, significant differences in the optical absorption due to dose rate are not observed.

Absorption for energies ~6 eV in the samples with doses $\geq 3.0 \times 10^{16}$ ions/cm^2 is due to the same defects produced at doses $\leq 1.0 \times 10^{16}$ ions/cm^2. Increasing the dose rate results in larger colloids and, hence, a greater disruption of the substrate network. This greater disruption of the network results in more defects which, in turn, causes more absorption at energies ≥ 5.0 with increasing dose rate. A similar increase in absorption for energies ~6 eV has been reported by Magruder, et al.,[11] with increasing nominal dose of Cu implantation in silica.

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CONCLUSIONS

1. Bimodal distribution of the Cu is not affected by dose rate for the range of dose rates examined in this work.
2. The increase in optical absorption for doses $\geq 3.0 \times 10^{16}$ at energies between 2 and 3.6 eV with increasing dose rate is attributed to increases in nucleation and growth of colloids.
3. The increase in EC is due to the increase in size of the colloids with increasing dose rate.
4. The absorption at energies ~6 eV is due to defects produced by the ion implantation process.

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FIGURE CAPTIONS

Figure 1: Ion backscattering depth profiles. Dose rates ($\mu A/cm^2$) are 0.7 for 4.9×10^{16} dose, 7.5 for 5.1×10^{16} dose, 2.6 and 7.5 for 2.5×10^{16} doses and 2.6 for 1.0×10^{16} dose.

Figure 2: Extinction coefficient as a function of energy for samples with nominal dose of 6.0×10^{16} ions/cm^2 for dose rates of (a) 0.7, (b) 2.6, (c) 5, and (d) 7.5 $\mu A/cm^2$.

Figure 3: Extinction coefficient as a function of energy for samples with nominal dose of 3.0×10^{16} ions/cm^2 for dose rates (a) 2.6 and (b) 7.5 $\mu A/cm^2$.

Figure 4: Extinction coefficient as a function of energy for samples with nominal dose 1.0×10^{16} ions/cm^2 for dose rates (a) 2.6 and (b) 7.5 $\mu A/cm^2$.

Table I

Table of Dose Rates Used for each Nominal Dose

Nominal Dose (ions/cm^2)	Dose Rate ($\mu A/cm^2$)
6×10^{16}	0.7, 2.6, 5, 7.5
3×10^{16}	2.6, 7.5
1×10^{16}	2.6, 7.5

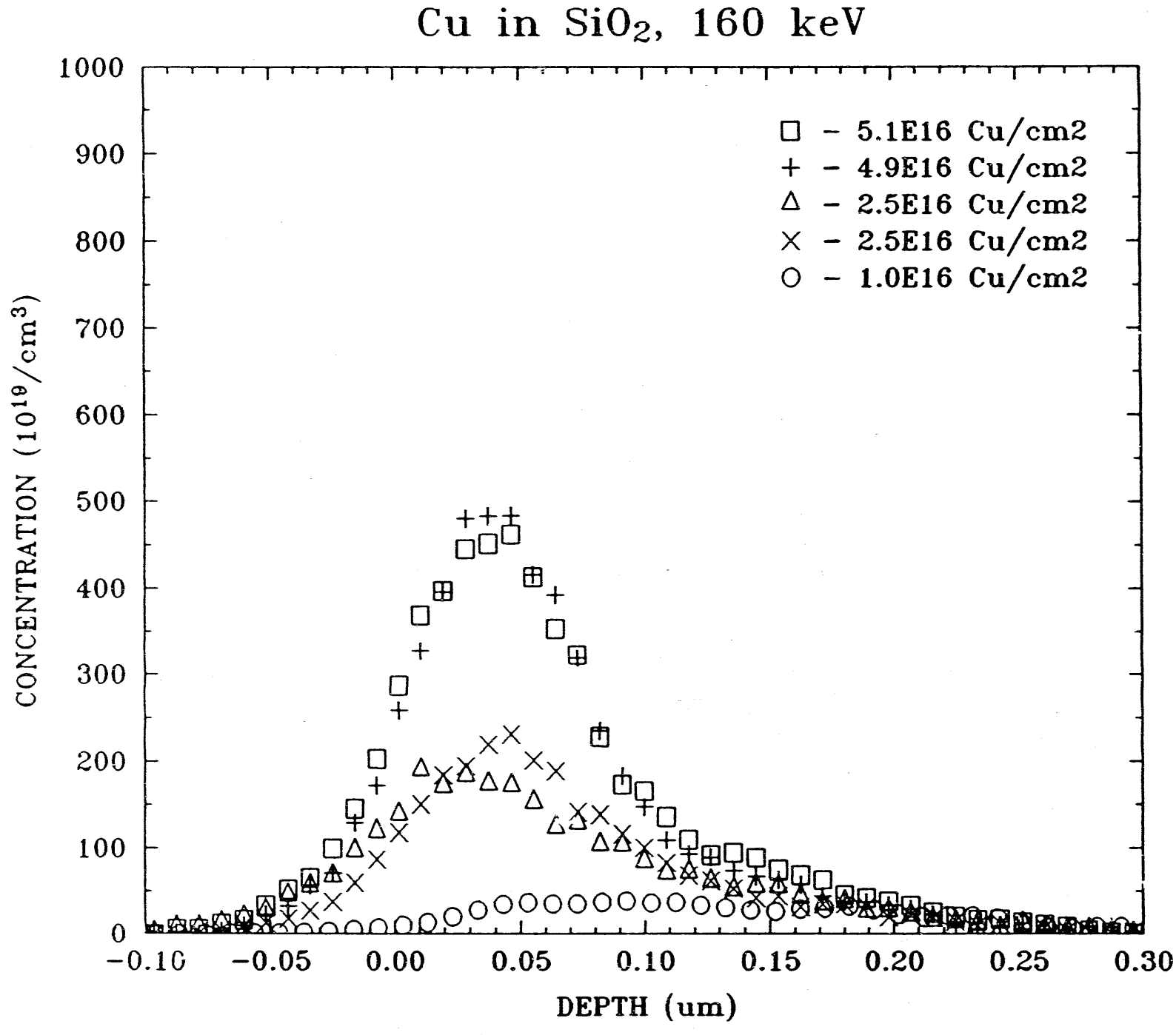
Cu in SiO2, 160 keV
□ - 5.1E16 Cu/cm2
+ - 4.9E16 Cu/cm2
△ - 2.5E16 Cu/cm2
× - 2.5E16 Cu/cm2
○ - 1.0E16 Cu/cm2
CONCENTRATION (10^19/cm^3)
1000
900
800
700
600
500
400
300
200
100
0
-0.10
-0.05
0.00
0.05
0.10
0.15
0.20
0.25
0.30
DEPTH (um)

Fig 1

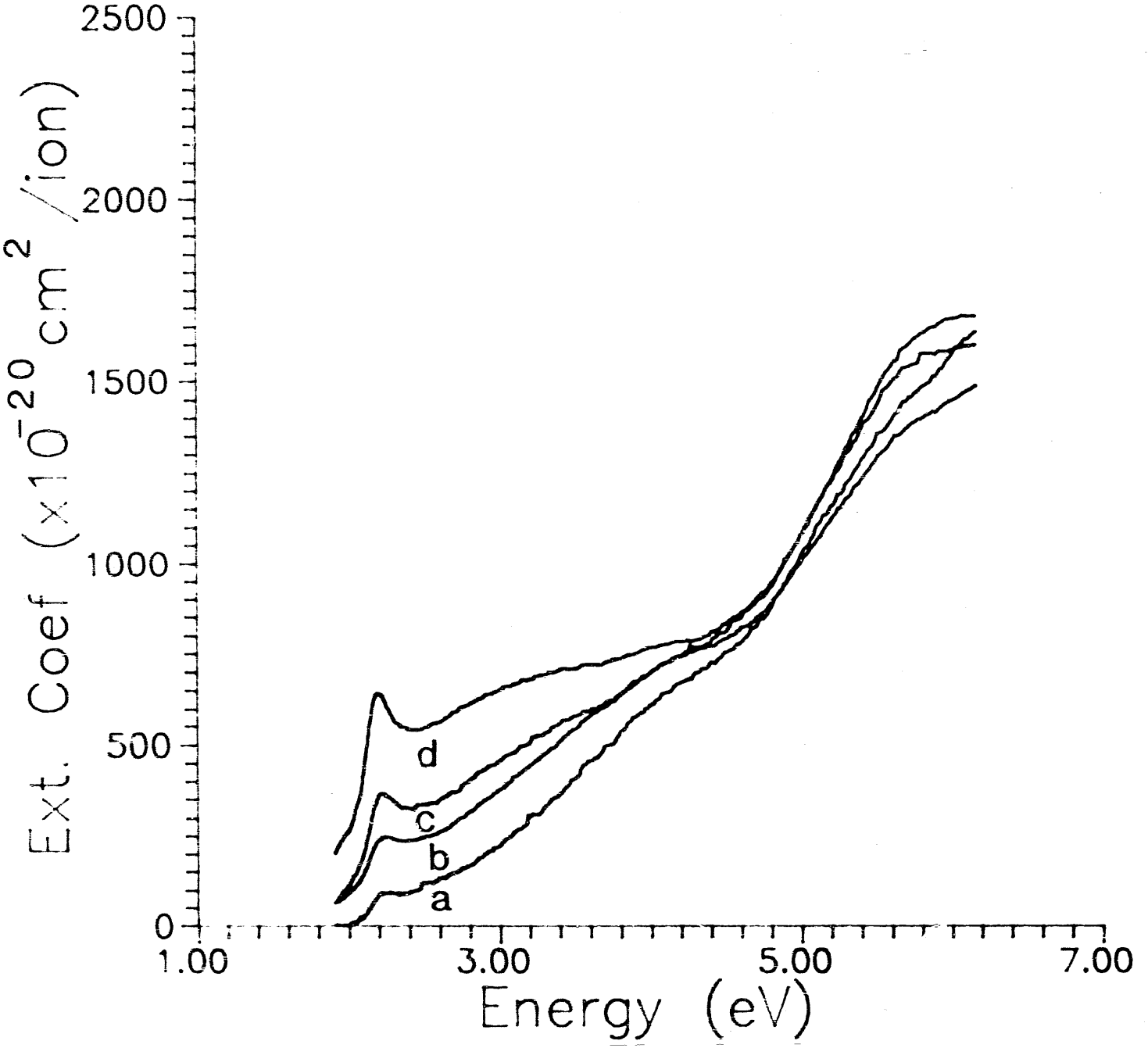
2500
2000
1500
1000
500
0
Ext. Coef ($\times 10^{-20}$ cm^2 /ion)
1.00
3.00
5.00
7.00
Energy (eV)
a
b
c
d

Fig 2

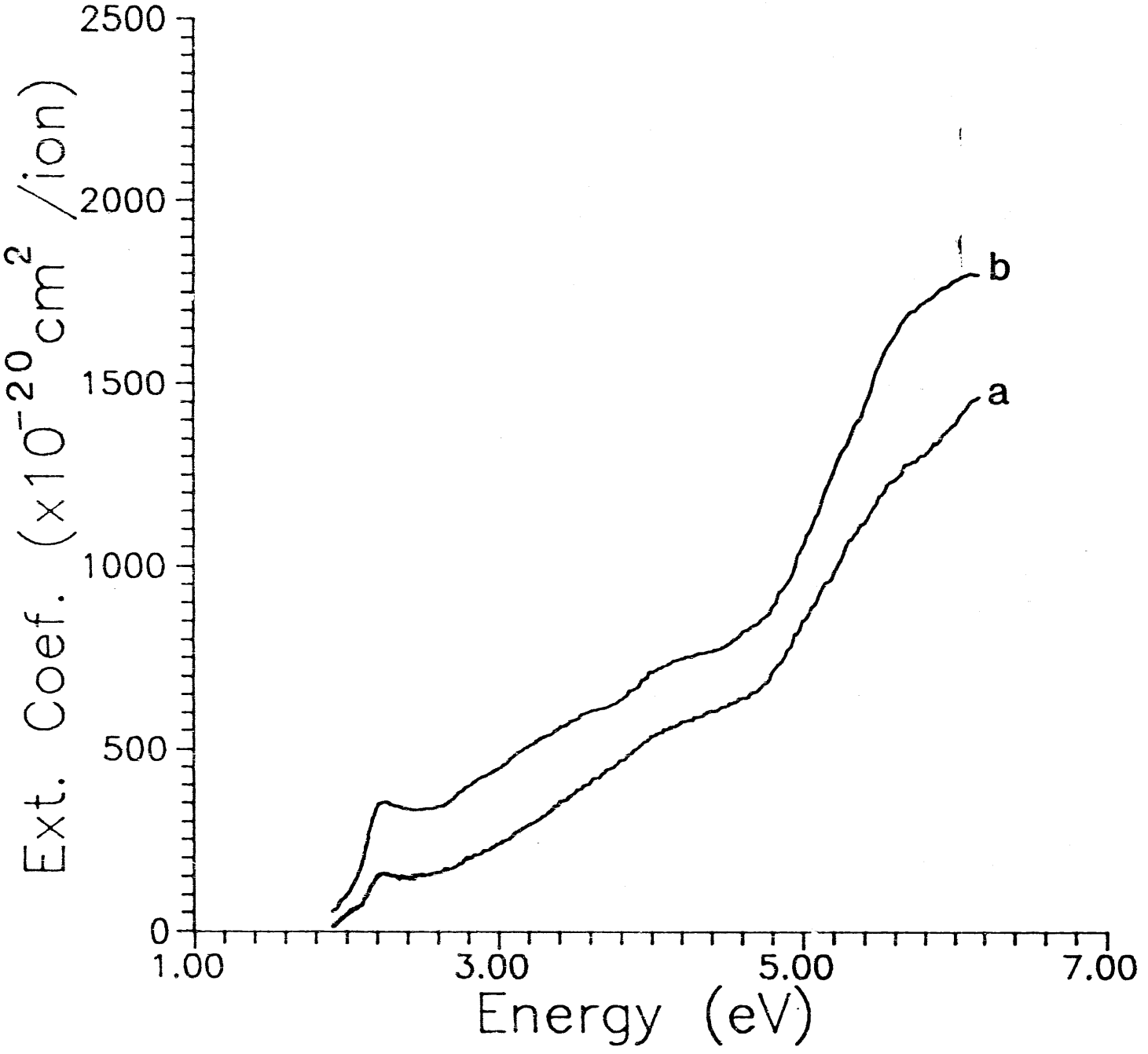
2500
2000
1500
1000
500
0
Ext. Coef. (x10^{-20}cm^2 /ion)
1.00
3.00
5.00
7.00
Energy (eV)
b
a

Fig 3

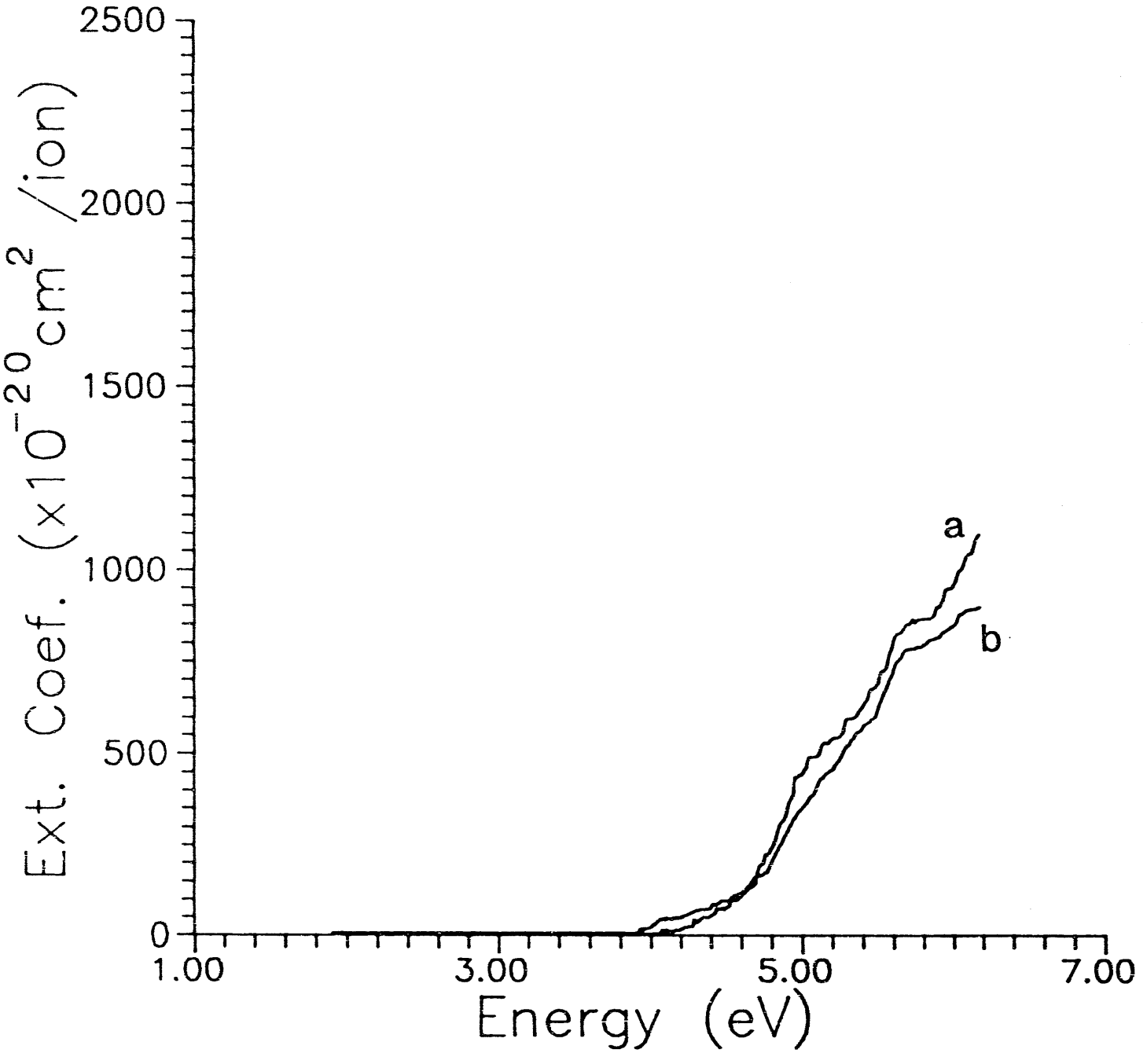
2500
2000
1500
1000
500
0
Ext. Coef. (x10^{-20}cm^2 /ion)
1.00
3.00
5.00
7.00
Energy (eV)
a
b

Fig 4

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