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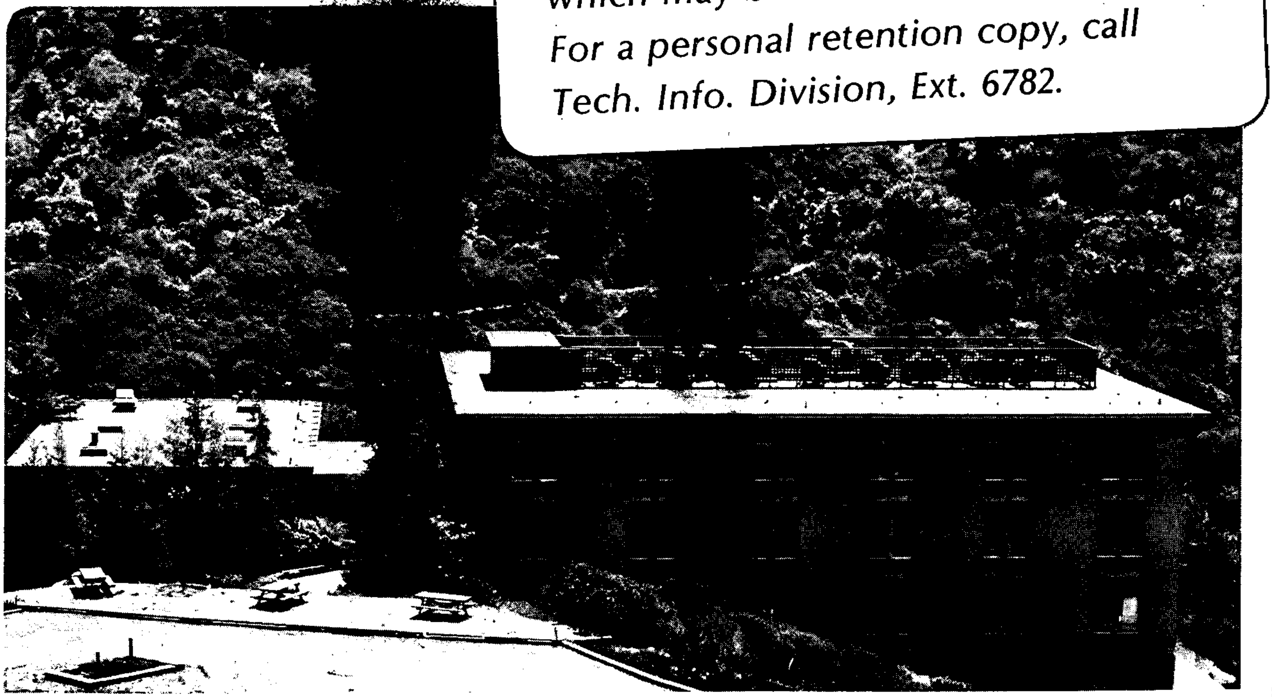

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DIRECT EVIDENCE OF ARSENIC CLUSTERING IN HIGH DOSE ARSENIC IMPLANTED SILICON

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ABSTRACT

High dose (5-7.5 x 10^{15} cm^{-2}) arsenic implantation was conducted in the energy range 50-120 keV into three types of (100) Si substrates: (i) bare Si, (ii) with a thermally grown screen-oxide (775Å), and (iii) pre-amorphized surface layer produced by self-implantation. The substrates were subsequently furnace annealed at 600°C in N_2. Cross-section transmission electron microscopy (XTEM) revealed that in all cases discrete layers of As related clusters and small dislocation loops occurred at depths matching the projected ranges of As into the Si substrates and original amorphous/crystalline interfaces respectively. The atomic profiles of As obtained by secondary ion mass spectrometry (SIMS) from these samples did not show any redistribution of As. The carrier concentration profiles from the spreading resistance measurements indicate that only 30 percent of As was electrically active. Comparison of XTEM and SIMS suggests that nucleation of the clusters occurred in the regions where As was present above the solid solubility limit in Si. The presence of recoiled oxygen has been found to stabilize the clusters.

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Although arsenic has been used as one of the main n-type dopants in Si, its electrical behavior both in diffused and implanted/annealed layers of Si, especially at high concentrations (greater than 10^{20} cm^{-3}) is not well understood. It has been found that the location of As atoms in the Si lattice and the accompanying electrical behavior at high concentrations is a complicated function of diffusion temperature.(1-3) An extreme example of this behavior has been demonstrated by a continuous wave laser annealing experiment where As could be completely activated to concentrations of 10^{21} cm^{-3}, i.e., in excess of its solid solubility limit in Si.(4,5) However, when these laser annealed samples were subsequently annealed in a furnace in the temperature range 700-1100°C, relaxation of the metastable arsenic concentration occurred reducing the carrier concentration by 8 to 10 times.(4,5) Similar results have been reported in the literature for samples that were first heated in a furnace to temperatures of 1000°C followed by a lower temperature heat treatment in the range 400-800°C.(6) Rutherford backscattering (RBS)/channeling studies show that under these conditions, the non-substitutional fraction of As increases, supporting the electrical data.(2) Transmission electron microscopy (TEM) results revealed that in addition to dislocations, dot-like defects were present in high concentration As diffused or implanted Si.(1,7) These latter defects have been attributed to As, although their precise nature and depth distribution could not be determined. In the present study, the depth distribution of As related defects in As implanted and low temperature annealed samples have been obtained by cross-sectional TEM and these results have been directly compared with atomic As and carrier concentration distributions. The effect of recoiled oxygen on stabilization of the defects has also been considered.

Arsenic ions of 50-120 keV were implanted in the dose range 5-7.5 x 10^{15} cm^{-2} at room temperature into three types of (100) Si samples: I. with a native oxide (bare Si), II. with a pre-amorphized surface layer produced by self-implantation and III. with a thermally grown oxide layer. The subsequent annealing was carried out in a furnace at 600°C for 15-30 minutes in a N_2 ambient. The results from higher temperature (1000°C) annealed samples have been described before.(8,9) The structural defect distributions in plan and cross-sectional (X) views were obtained by TEM in both the bright-field and dark-field/weak-beam modes. The depth distributions of As, recoiled oxygen and electrical carriers were obtained by secondary ion mass spectrometry and spreading resistance methods, respectively.

The XTEM results from the implanted but unannealed type I sample (5 x 10^{15} cm^{-2}, 100keV) showed a continuous amorphous layer, 1250Å wide, extending to the surface (Fig. 1a). The corresponding As distribution from this sample was gaussian with peaks occurring at 600Å (Fig. 2). The XTEM results from the 600°C annealed sample showed an interesting recrystallization behavior of the amorphous layer: two discrete layers of defects (A and B, Fig. 1b) were created at mean depths of 600Å and 1300Å. The location of the defect layers corresponded precisely to the projected range (Rp) of 100 keV As and the depth of the original amorphous/crystalline interface (Fig. 1a). The SIMS profile of the As obtained after the annealing did not show any redistribution and was the same as the unannealed sample (Fig. 2). The electrical carrier profile followed the atomic As profile but with reduced activation. The peak carrier concentration was 10^{20} cm^{-3} and only 30 percent of the As atoms was found to be electrically active. Higher electrical activity has been reported for lower dose (10^{15} cm^{-2}) As implanted and 550°C annealed Si sample.(10)

The regrowth of an amorphous layer in As implanted (100) Si on subsequent annealing can produce defect free material so long as the amorphous/crystalline interface is sharp and concentration is low (below solid solubility limit).(7) However, straggling ion damage immediately below the amorphous/crystalline interface appear as small dislocation loops on annealing.(11,12) The occurrence of the defect clusters at Rp in Fig. 1b indicates that the As in this region has exceeded the solid solubility limit. The As is probably rejected in front of the advancing amorphous/ crystalline interface eventually resulting in precipitation during recrystallization. That the clustering at Rp is indeed related to As has been further confirmed by the XTEM results from type II and type III samples described below.

For type II substrate, a 1860Å wide amorphous layer was first created by self-implantation (100 keV, 2 x 10^{15} cm^{-2} and LN_2 temperature implant), then As was subsequently introduced at room temperature either at 50 or 100 keV again to doses of 5 x 10^{15} cm^{-2}. Furnace annealing of these samples at 600°C again created two discrete layers of defect clusters (Fig. 3). However, while the deeper layer of the clusters in both cases occurred at 1900Å, i.e., at a depth that corresponded to the amorphous/crystalline interface in the pre-amorphized sample, the near-surface layer of the clusters appeared at mean depths of 230Å and 470Å that were located in the vicinity of the projected ranges of As corresponding to 50 and 100 keV implantations, respectively.

For type III substrate, As was implanted through a 775Å thick oxide layer (7.5 x 10^{15} cm^{-2}, 120 keV) such that approximately 50 percent As was stopped in the oxide layer and the Rp of the As coincided with the SiO_2/Si interface. The unannealed sample showed a continuous amorphous layer of 750Å extending from the SiO_2/Si interface (Fig. 4a). The 600°C furnace anneal created only one discrete layer of small dislocation loops in this case which was located at a mean depth of 830Å (Fig. 4b). The position of the loops again corresponded closely to the amorphous/crystalline interface in Fig. 4a. From the width of the recrystallized region, it appears either the amorphous layer did not fully recrystallize or a dense band of small clusters is present at the SiO_2/Si interface. Further work is underway to clarify the nature of this surface damage.

The measured width of the near-surface layer of the clusters in Fig. 1b and the SIMS As data from Fig. 2 suggests that the As solubility limit in Si at 600°C is $\sim 3 \times 10^{20}$ cm^{-3}. Weak-beam TEM micrographs taken from a plan view specimen corresponding to Figs. 1b (not included here) show that in addition to the clusters observed (~100Å diameter) at Rp in the XTEM micrographs, a high density of smaller clusters (≤50Å diameter) extend closer to the surface above Rp.(8) Such clusters are hard to detect in XTEM micrographs of cross-section specimens even under weak-beam diffraction conditions. This is because XTEM specimen preparation requires ion milling at 6-10 keV and the damage introduced due to the milling obscures the contrast from such small clusters. The plan view micrographs, on the other hand, are obtained from chemically thinned specimens which have a clear background under weak-beam TEM conditions. If the smaller clusters do also involve As, the solubility limit of As may be lower than 3×10^{20} cm^{-3}. The electrical data shows that the maximum carrier concentration between the surface and Rp is only 10^{20} cm^{-3}, which is consistent with the assumption that the smaller clusters are As related precipitates.

From the SIMS results and diffusivity data, the diffusion length of As in Si at 600°C should be negligible (<10Å). The mean diameter of As-rich clusters as observed in Figs. 1b, 3a and 3b is ~100Å, which suggests that the precipitation process involved enhanced diffusion within the migrating amorphous-crystalline interface where the diffusion length of As could be expected to be higher than in the single crystal. The regrowth rate of amorphous silicon heavily implanted with As (2×10^{15} cm^{-2} at 80 keV) has been shown to decrease by a factor of 6 compared to pure silicon(13) which is also consistent with pile-up of excess As of the amorphous/crystalline interface.

The growth and coarsening of the dislocation loops in the deeper layers for annealing temperatures of up to 1000°C were found to be significantly different than the near-surface layer of As rich clusters.(8) In type I samples, the dislocation loops in layer B (Fig. 1b) grew rapidly in size (10 times or more) and glided to the surface while the clusters showed only a small increase in average size (x 2) at 1000°C.(8) However, in type III sample, although the loops grew in size (8 to 10 times) at 1000°C they could no longer glide to the surface. The shape of the loops was also quite irregular indicating that they were heavily pinned. From the SIMS profile in Fig. 2, the concentrations of recoiled oxygen at the layers A and B (Fig. 1b) were determined to be 10^{19} cm^{-3} and 7×10^{18} cm^{-3} respectively, which were above the solid solubility limit of oxygen in Si. This indicates that the oxygen probably plays an important role in restricting the growth of the As-rich precipitates and dislocation loops even in the case of bare Si implanted samples. The pinning of the defects occurs presumably by fine Si-0 complexes (~20Å diameter). The gettering of 0 to the loops in the deeper layer has been demonstrated previously.(9) From these results, it would be expected that the fine clusters observed above the upper layers in Figs. 1b, 3a and 3b are also affected by the presence of recoiled-oxygen because of its high concentration ($>10^{20}$ cm^{-3}) in this region.

In summary, (1) direct evidence of As clustering has been obtained by cross-sectional TEM in high-dose As implanted (100) Si. The solid solubility limit of As from these results was found to be $\sim 3 \times 10^{20}$ cm^{-3} at 600°C, (2) the highest electrical carrier concentration in 600°C annealed samples was $\sim 10^{20}$ cm^{-3} and (3) the presence of recoiled oxygen restricted the coarsening of As-rich clusters/precipitates.

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FIGURE CAPTIONS

Figure 1

As^+ ---> (100) Si, 5 x 10^{15} cm^{-2}, 100keV, room temperature implant (type I). XTEM micrographs showing (a) a continuous amorphous layer (dark band) extending to the surface (unannealed sample) and (b) two discrete layers of defects, A and B, corresponding to the Rp and amorphous/crystalline interface in Fig. 1a (600°C/30 mins., N_2 annealed sample).

Figure 2

Arsenic (SIMS), recoiled oxygen (SIMS) and carrier concentration (spreading resistance) profiles from the samples of Fig. 1.

Figure 3

As^+ ---> (100) Si with a self-implantation induces 1860Å wide amorphous surface layer, 5 x 10^{15} cm^{-2}, room temperature implant (type II), furnace annealed at 600°C for 30 minutes in N_2. XTEM micrographs showing location of two discrete layers of defects in (a) 50keV and (b) 100keV As^+ implanted samples. Note the positions of the upper layers in (a) and (b) changes according to the Rps of As^+ but the lower layers remain at the same depth in the two cases.

Figure 4

As^+ ---> SiO_2 (775Å)/(100)Si, 7.5 x 10^{15} cm^{-2}, 120keV, room temperature implant (type III). XTEM micrographs showing (a) the oxide layer and a 750Å wide continuous amorphous layer extending to the SiO_2/Si interface (unannealed sample) and (b) a discrete layer of defects at 830Å, corresponding closely to the amorphous/crystalline interface in Fig. 4a (600°C/15mins., N_2 annealed sample).

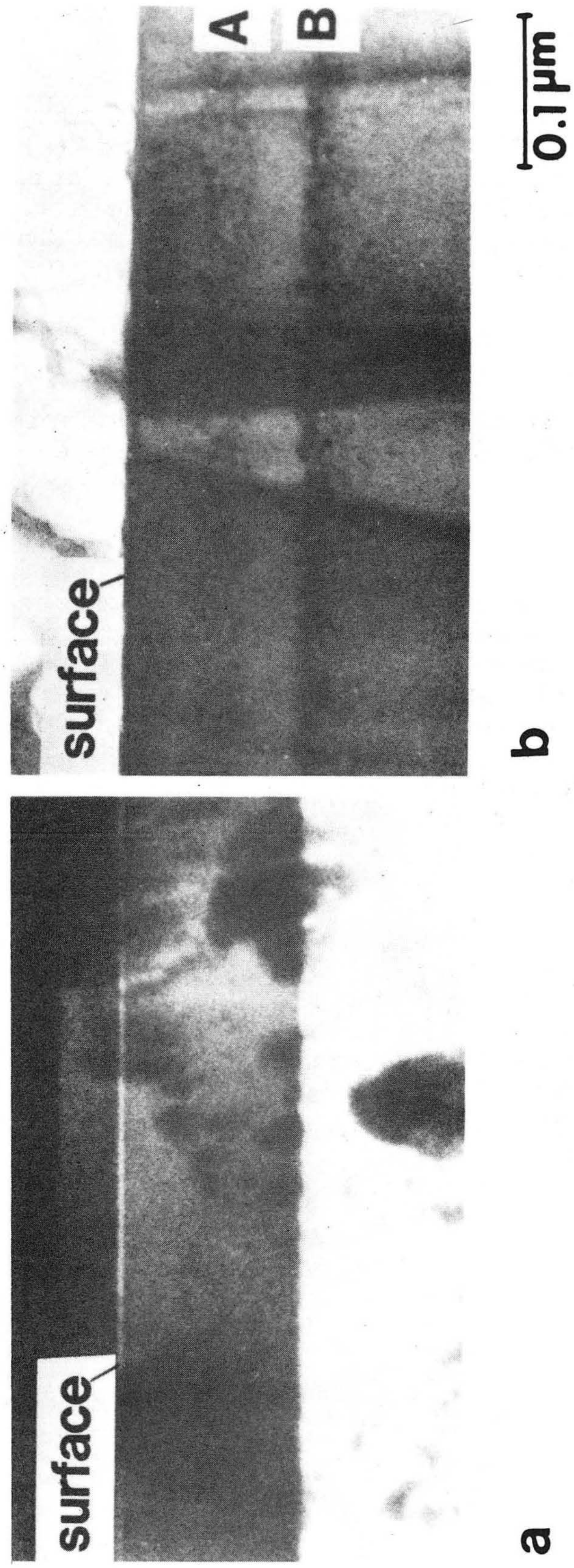

Figure 1

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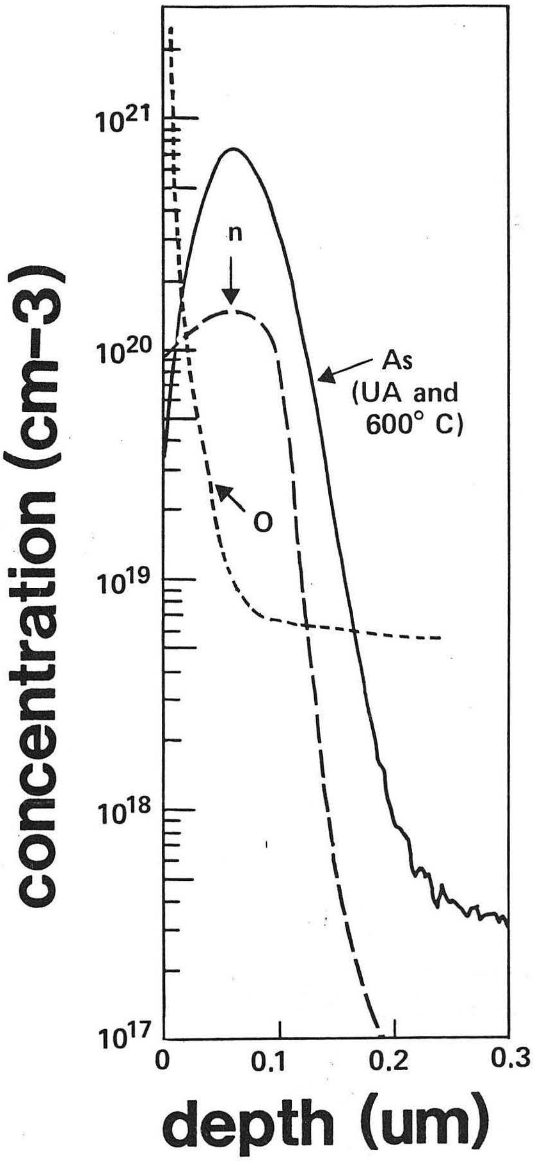
concentration (cm-3)
10^{21}
10^{20}
10^{19}
10^{18}
10^{17}
n
As
(UA and
600° C)
O
0
0.1
0.2
0.3
depth (um)

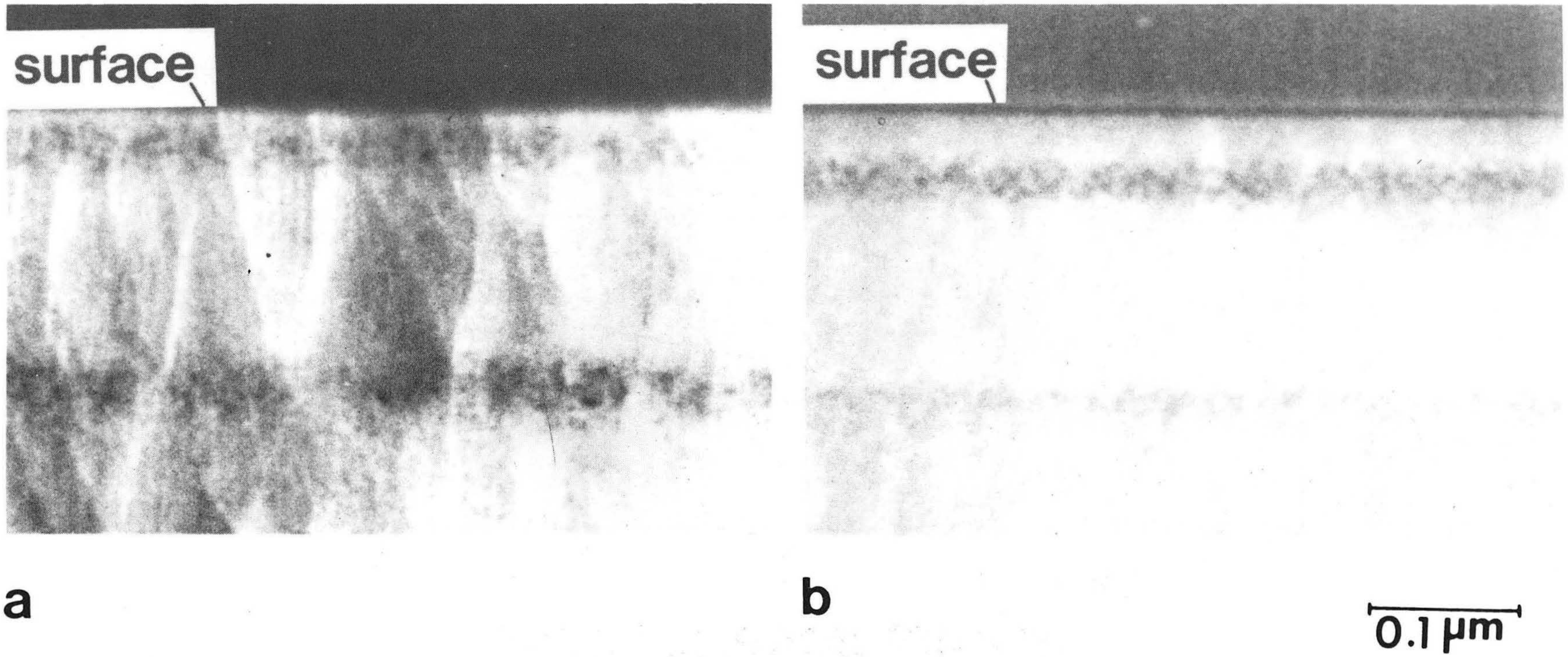

Figure 3

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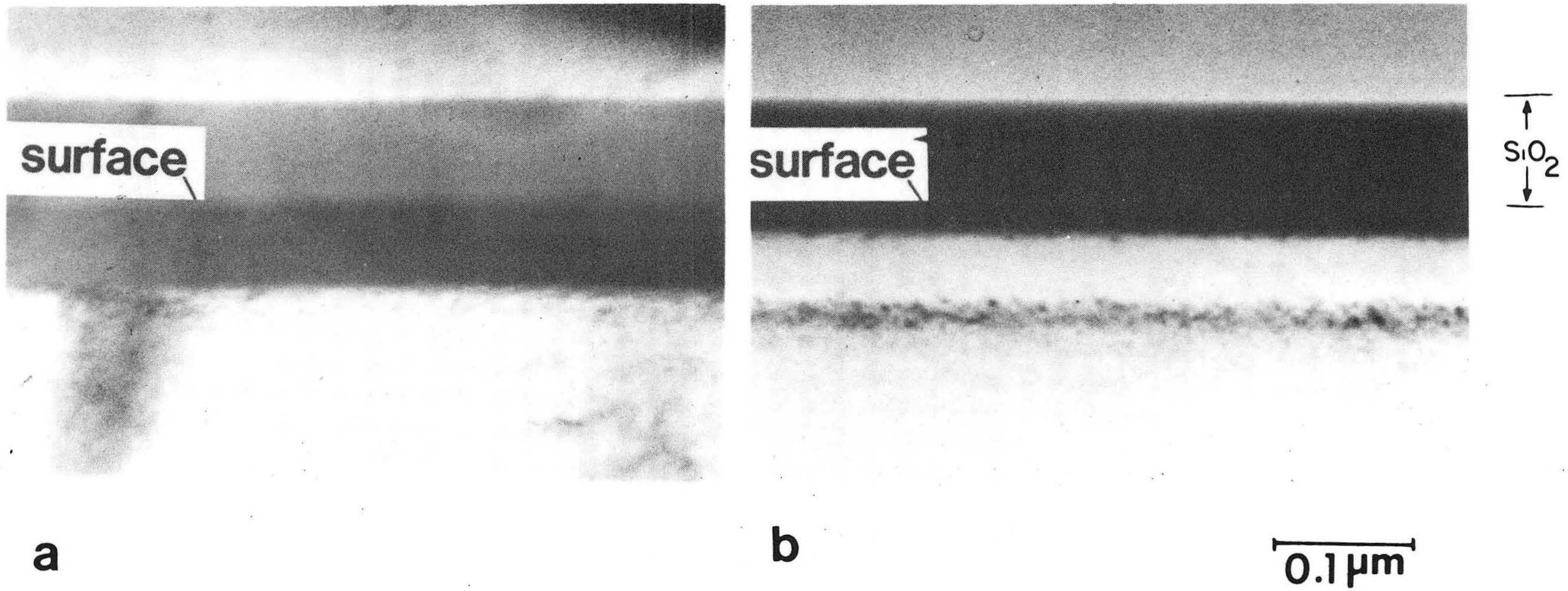

Figure 4

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