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November 1983

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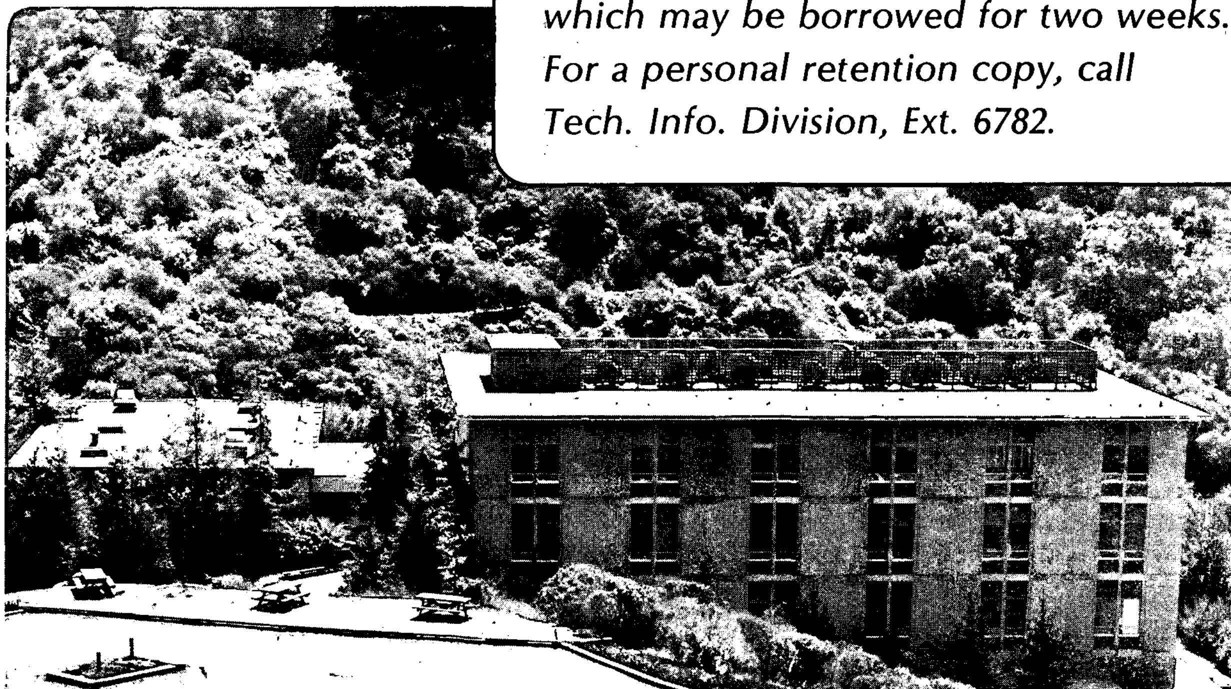

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HIGH RESOLUTION TEM STUDIES OF DEFECTS NEAR $Si-SiO_2$ INTERFACE

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ABSTRACT

Small defects with habit parallel to {100} and {311} matrix planes were observed using high resolution transmission electron microscopy (HREM) within 100 nm from the $Si-SiO_2$ interfaces after one step oxidation in dry O_2 at 900°C, 1000°C and 1150°C of Czochralski (CZ) grown [100] p-type boron doped, 1.5 - 20 Ω cm Si wafers with concentrations of oxygen $1.4 \times 10^{18} cm^{-3}$ and carbon $4. - 10. \times 10^{16} cm^{-3}$. The defects were less than 10 nm wide and 1 nm thick. The {100} and {311} defect are interpreted tentatively as thin silica plateletes and {311} stacking faults respectively. Distribution of defects near the interface was random although their density appeared to be lower for higher oxidation temperatures. It is not yet clear whether the defects were formed during the oxidation treatments or were present near the surfaces of the as-received wafers.

INTRODUCTION

Silicon crystals grown from quartz crucibles by the Czochralski method typically contain $10^{18} cm^{-3}$ interstitially dissolved oxygen. This corresponds approximately to the oxygen solid solubility limit at the melting temperature. Thus during processing steps in production of electronic devices involving lower temperature heat treatments, oxygen precipitation from supersaturated solid solution can result [1]. The defects formed are beneficial for gettering metallic impurities if they are away from the active device regions [2,3,4]. However the presence of precipitates within active regions of the devices can be detrimental to performance. For example, higher generation current has been observed in MOS capacitors if these defects are found within the depletion region [5] or near p-n junctions [6]. In this paper, preliminary observations of defects within the depth of the depletion width from the $Si-SiO_2$ interface are reported in wafers after a one-step oxidation at temperatures above 900°C.

The defects were observed during a systematic investigation of the $Si-SiO_2$ interface structure using lattice imaging electron microscopy of cross-sectional specimens.

EXPERIMENTAL PROCEDURES

Commercially supplied (without specification of thermal history) Czochralski-grown Si [100] wafers, p-type boron doped 1.5 - 20 cm were used for oxidation. These wafers contained $1.4 \times 10^{18} cm^{-3}$ oxygen and 4 to $10 \times 10^{16} cm^{-3}$ of carbon atoms as estimated from I.R. measurements.

The wafers were cleaned in a series of rinses including: (1) 5:1:1 H_2O: NH_4OH:H_2O_2, (2) deionized water (D.I.), (3) 5:1:1 H_2O:HCl:H_2O_2, (4) D.I., (5) 50:1 H_2O:HF, (6) D.I., and after drying in N_2 were transferred into the furnace with an argon atmosphere. After five minutes the argon was replaced by dry oxygen for the desired time. The wafers were removed from the hot zone of the furnace after again changing to argon ambient during a two minute interval. The oxidations were performed at 900°C, 1000°C, and 1150°C, for times necessary to grow oxide layers 20 nm to 100 nm thick.

Cross-sectional TEM specimens were prepared using the standard technique [7]. High resolution TEM images were obtained using a JEM 200 CX electron microscope operating at 200 kV and equipped with high resolution pole piece. The electron beam parallel to the zone axis [011] allowed resolution of two sets of {111} planes in the silicon crystal edge on. The distance between {111} fringes corresponds to the distance 0.314 nm spacing of silicon {111} lattice planes.

EXPERIMENTAL RESULTS AND DISCUSSION

Observations in the vicinity of the Si-SiO_2 interface within a distance of about one micron were performed on the first set of specimens with about 200 nm of oxide grown at 900°C for 120 minutes. Two characteristic classes of defects were observed and are shown in Fig. 1. The defects marked "a" in Fig. 1 are tentatively interpreted as silica precipitate platelets growing on 100 matrix planes. Larger defects having similar contrast have been observed in plan view silicon specimens prepared from CZ silicon crystals after anneals at 870°C and 650°C and are commonly known as "black dot" defects [8,9]. Figs. 2 and 3 show higher magnifications of platelet defects marked in Fig. 1 by "a_1", and "a_2" respectively. The observed dimensions varied from 4 nm to 10 nm. The thickness was estimated to be 0.3 - 0.6 nm. A second type of defects which appeared occasionally near the platelets are indicated by "b" in Figs. 1, 3. These defects are parallel to {311} matrix planes. They also have been previously observed in CZ silicon and have been called {311} stacking faults [10]. Other authors [8,9] have considered them to be

precipitates growing on the {311} matrix planes. They may be elongated in the <110> direction parallel to the beam and thus observed as a cross section 3-4 nm in width [11]. The density of the {311} defects appeared to be lower than that of the platelets and the distribution of both types of defects appeared to be random within about 100 nm from the $Si-SiO_2$ interface.

For the wafers oxidized at 1000°C for eight minutes similar defects were also observed. Figure 4 shows two {100} precipitates within 15 nm of the $Si-SiO_2$ interface. The dimensions and contrast are similar to the "a" defects observed at 900°. The {311} defects were also observed at a somewhat greater distance from the $Si-SiO_2$ interface. The density of both defects was lower than in the specimen oxidized at 900°C.

Specimens oxidized at 1150°C for 25 minutes also contained similar defects as shown in Fig. 5. The density of {100} defects was considerably smaller than at 900°C and 1000°C.

To begin to establish the origin of these defects, observations were performed on cross sections of as-supplied wafers. The high resolution image of such a specimen is shown in Fig. 6. Within the area studied, a few defects were observed with similar contrast to the {311} stacking faults although smaller in size. This observation suggests that some or all of the defects may have been present in the as-received wafers. Because the density of these defects may vary markedly from one wafer to another, or from one part to another in a single wafer, it is not yet possible to conclude that these defects were formed during the oxidation treatment.

However, it is of interest that after an oxidizing anneal even at 1150°, these defects are still present very near the surface.

ACKNOWLEDGEMENTS

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FIGURE CAPTIONS

Fig. 1 HREM image of the defects near $Si-SiO_2$ interface after 900°C oxidation.

Fig. 2 Higher magnification HREM image of {100} defect marked a_1 in Fig. 1.

Fig. 3 Higher magnification HREM image of {100} and {311} defects marked a_2 and b_1, b_2 in Fig. 1.

Fig. 4 HREM image of the {100} defects near the $Si-SiO_2$ interface (after 1000°C oxidation).

Fig. 5 HREM image of the {311} defect near the interface (after 1150°C oxidation).

Fig. 6 HREM image of the defect in as-supplied wafer.

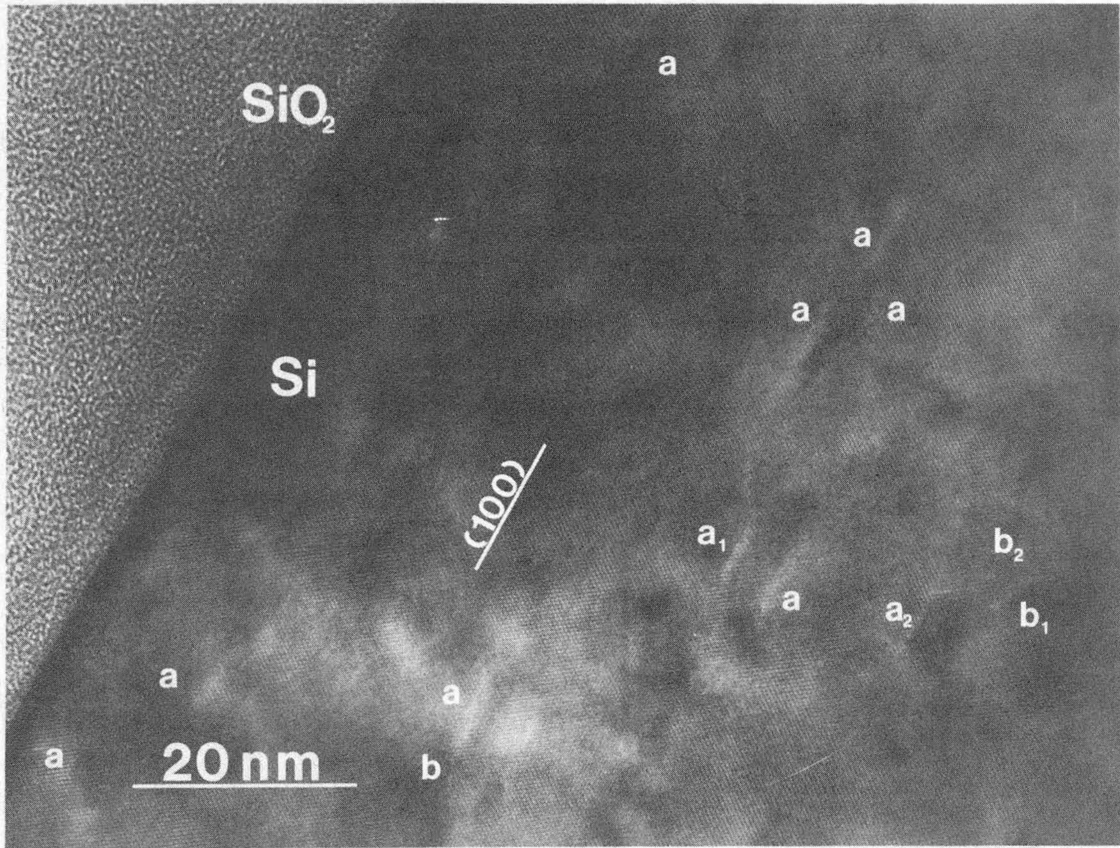

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Fig. 1

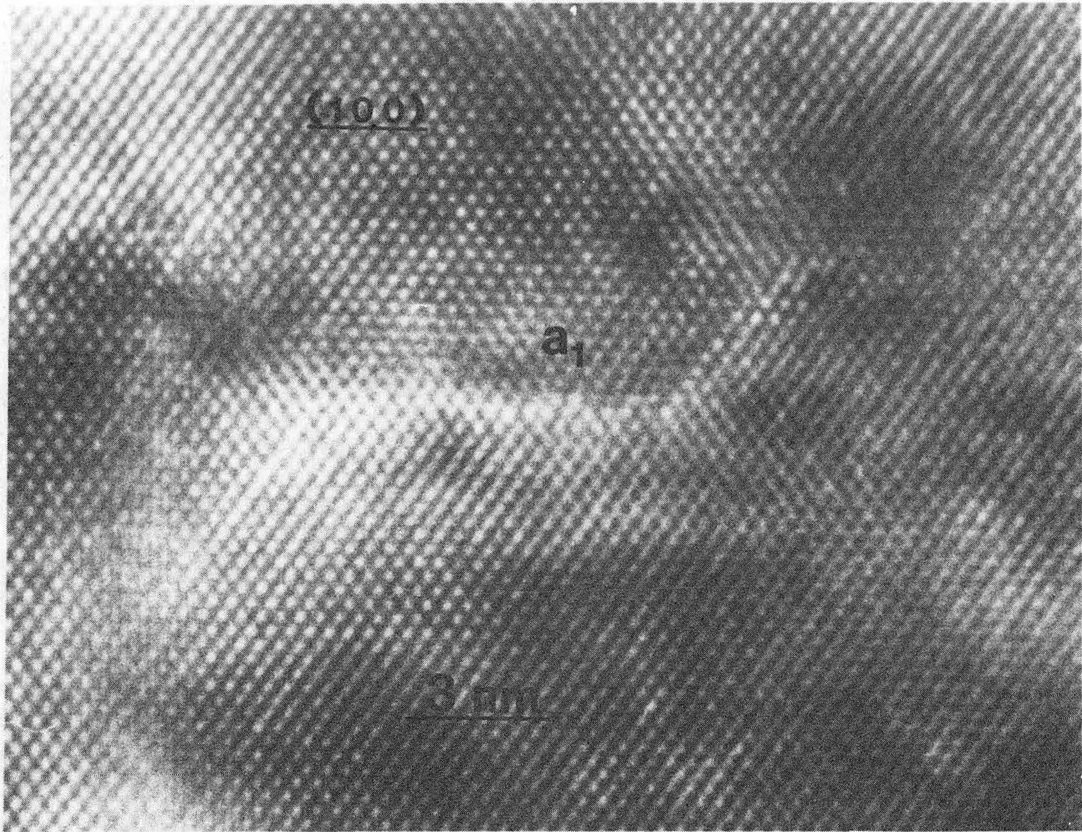

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Fig. 2

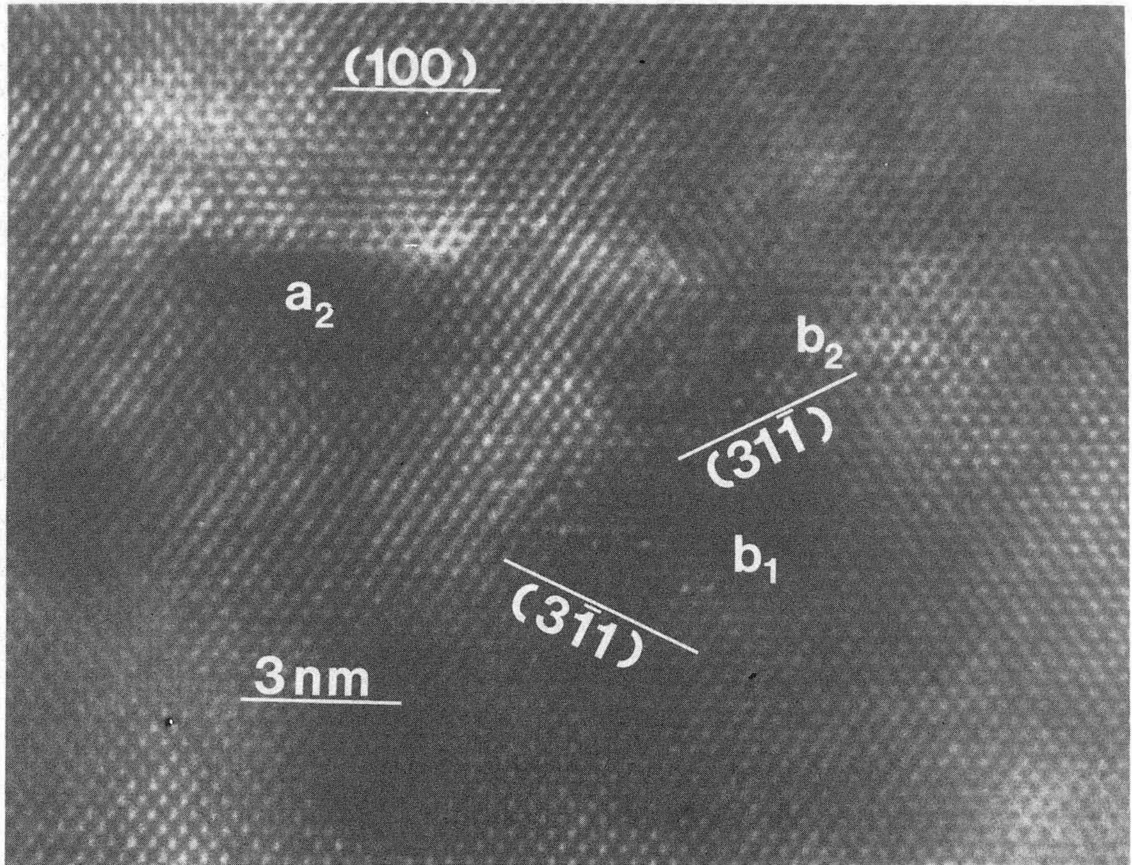

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Fig. 3

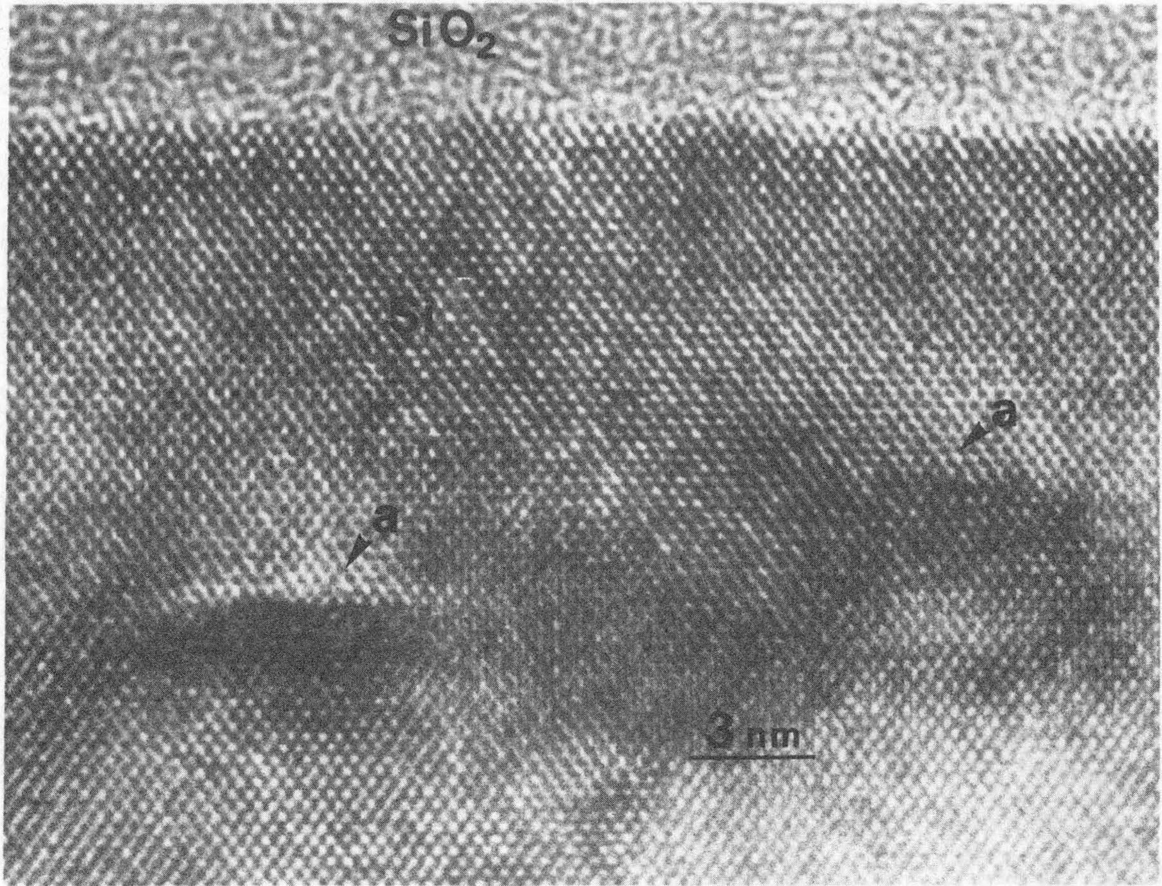

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Fig. 4

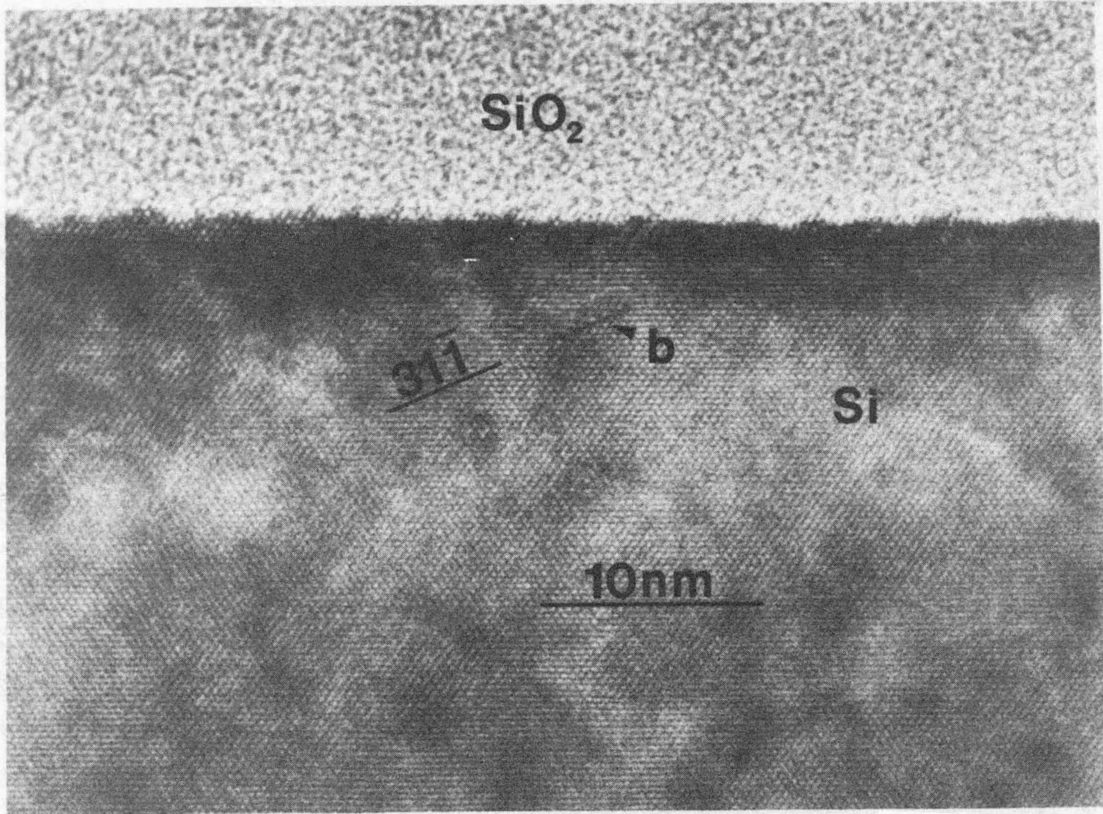

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Fig. 5

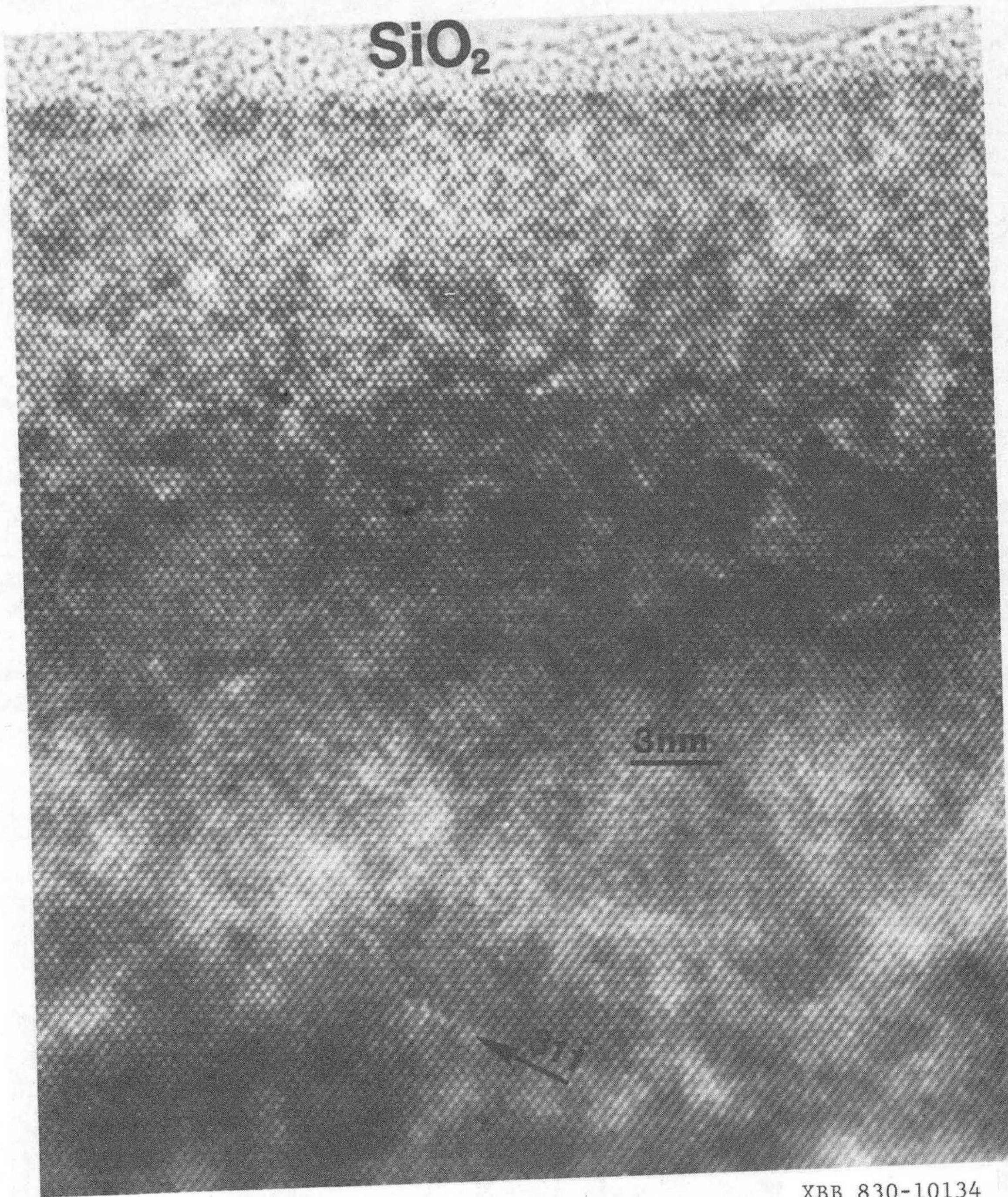

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Fig. 6

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