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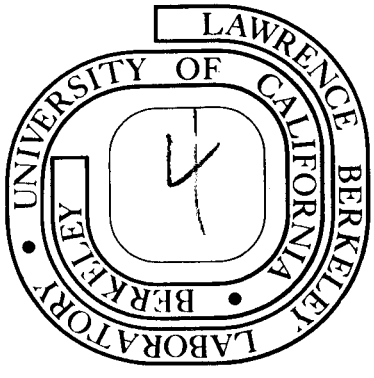

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DISCLAIMER

A HIGH RESOLUTION ELECTRON MICROSCOPY STUDY OF THE Si - SiO_2 INTERFACE

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ABSTRACT

The structure of (100), (111) and (911) interfaces between Si and thermally grown, dry SiO_2 has been studied in cross-section by high resolution electron microscopy (HREM), at about 3Å resolution. The three types of interfaces have been found to be rather similar. The Si crystal transforms into the amorphous oxide quite abruptly - within about 3Å. One plane high atomic steps exist on the Si surface, separated by typically 20-40Å. They produce a surface roughness of about 4Å over distances of around 50Å. Most interfaces also show a longer range modulation of a height of ∿4-8Å, with a wavelength of 200-500Å. No evidence of a transition region of a nonstoichiometric oxide has been found, and the 10Å-wide dark band reported by us after a preliminary investigation is shown to be an imaging artifact. However, the sensitivity of the HREM technique to changes in the composition of the amorphous oxide is relatively poor.

INTRODUCTION

The structure of the $Si-SiO_2$ interface has been studied by many different techniques. A transition region of nonstoichiometric oxide has always been found, but its width Δ tends to vary, roughly in proportion to the resolution of the technique used. Thus Δ = 600Å from Rutherford back-scattering,[1] 20Å from low energy ion back-scattering,[2] 35Å and later 10Å by Auger spectroscopy, [3,4] and 20Å by electron spectroscopy for chemical analysis.[5] Additional results on the interface structure have been deduced from surface free energy measurements,[6] and from the measurement of the electrical properties of the interface.[7]

High resolution electron microscopy has, since several years ago, been able to directly resolve the 3.2Å Si crystal lattice. It should give results of similar resolution on the interface structure. Blanc, Buiocchi, Abrahams and Ham[8] have recently used the EM technique, but their resolution was only about 10Å. They found the (100) interface to be smooth and free of Si protusions within this limit. Improving the resolution to 3Å yields several further results, as this study will demonstrate.

SPECIMEN PREPARATION AND THE EXPERIMENTAL TECHNIQUE

The oxides were between 1000 and 1500Å thick, and were grown on 10-30 Ωcm p-type Si wafers in dry air at 1100°C, and subsequently annealed in H_2 at 380°C. Typical peak mobilities at 4.2°K on MOSFETs made with identical oxides were 10,000-15,000 cm^2/Vsec on the (100) surface, 5000 cm^2/Vsec on (911), and about 1000 cm^2/Vsec on (111).

The thin cross-sections were prepared by cutting a slice normal to a [011] direction lying in the plane of the interface, thinning the slice mechanically to about 0.1 mm, ion beam milling till perforation at 7kV,

and finally by milling at 2kV and a low incidence angle to remove any surface damage. For protection of the surface oxide against the milling ions, several MOS devices were stacked on top of each other prior to the slicing, and bonded together with epoxy.

In the immediate vicinity of the hole through the MOS cross-section, the interface is only 100-200Å thick, and therefore ideally suited for HREM. A low magnification image of the prepared sample is shown in Fig. 1a.

The interfaces were examined in a Siemens 102 EM at 125kV and electron-optical magnifications of 3000x to 500,000x, using a doubly-tilting specimen holder to allow the proper orientation of the interface to be achieved. Mainly because of the poor coherence of the electron beam from our thermionic electron gun, the Si crystal lattice was only very poorly visible directly on the microscope screen and the finer details of the interface structure could only be studied on micrographs recorded with typically 6 sec. exposure. Planned improvements of the microscope performance should however enable us to observe the interface detail directly on the fluorescent screen.

IMAGE INTERPRETATION

The high energy electrons are scattered by the Si crystal into Bragg beams and by the oxide into diffuse rings. The electron microscope brings the diverging beams and the diffuse scattering back into coincidence. The resulting interference patterns between overlapping Bragg beams have the periodicity of the original lattice. A perfect imaging system would bring all the Bragg beams into the optimum coincidence for phase contrast imaging, and there would be a one-to-one correspondence between the image and the object. In practice, however, the coincidence can only be controlled by defocussing (changing the current through the electromagnetic objective

lens), and by tilting the main beam with respect to the optic axis. The optimum coincidence can therefore be achieved only for a strictly limited number of Bragg beams. Moreover, poor coherence of the incident electron beam frequently makes the lattice fringes invisible by destroying the interference altogether.

In most of the experiments to be described here, the interface was viewed along the [011] direction, and we have used axial illumination and defocus values of about -1400 to -1900Å. This brings the 111 diffracted beams (Fig. 1b) into optimum coincidence with the main beam,[9,10,11] and allows us to view the (111) planes as well as (200) and (220) planes with the minimum distortion possible in a microscope of the Siemens 102 type. Higher order planes are not visible due to the effects of limited coherence and microscope aberrations. Tilting the illumination so that the optic axis is half-way between the main beam and one of the Bragg beams reduces the coherence requirements, but the resulting image is likely to contain artifacts due to imperfect coincidence of the other beams.

STRUCTURE OF (100), (111) AND (911) INTERFACES

Fig. 2 shows four interfaces, imaged edge-on parallel to [011]. {111} planes are resolved by interference between the 111 beams and the main beam, {200} and {220} planes by interference among the 111 beams. One or the other type of lattice fringes may predominate depending on the specimen thickness and the exact imaging conditions.

The transition from the Si crystal into the oxide is quite abrupt, as can be best seen in a) and c), which were taken with axial illumination. The faint fringes above the crystal in b), and the dark band as well as the short fringes above it in d) are artifacts due to the use of tilted illumination. The tilted illumination however makes it easier to see the

the 3.2Å high (d_{111}) steps on the (111) surface, and the 1.4Å high (d_{400}) steps on (100). The images shown here are typical of 15 different interfaces examined though the (111) interface shown in b) is perhaps slightly rougher than average.

The surface steps are typically 20-40Å apart, and can therefore be seen directly only in the thinnest parts of the cross-section. However, since regions thinner than 100Å could be susceptible to damage from the ion milling and the electron irradiation, the images selected for Fig. 2 are from regions about 100-200Å thick (as measured from thickness fringes[12] and the variation in lattice fringes' contrast[13]), and therefore show the superposition of several steps. The ∿4Å roughness is however clearly visible up to thickness of ∿400Å, where projection smooths the roughness out.

LONG-RANGE MODULATION

On most interfaces we have found, in addition to the surface steps spaced by 20-40Å, a longer periodicity (Fig. 3). Its observation however requires that the ion milling produces a thin (less than 400Å) cross-section at least 1000Å long, and as this does not always happen, we are as yet unable to define precisely the conditions under which the modulation arises. So far it appears to be a general phenomenon, the modulation height being about 4-8Å, but the periodicity appears to vary from 200-300Å (911) to 500-600Å (111). Similar modulation of the same height, as well as the one-plane-high surface steps have been also observed in a preliminary investigation of much thicker wet oxides.

TRANSITION REGION

The structures seen in the image of the amorphous oxide are produced by the superposition of many atoms throughout the depth of the material, and cannot, except under extremely favorable circumstances,[14] be interpreted in terms of the detailed oxide structure. Moreover, the image of the amorphous region is very strongly dependent on defocus,[9] as shown in Fig. 4. Though the figure also shows some features at the interface that are relatively defocus-independent, ascribing these directly to small ($\sim$5Å diameter) inhomogeneities such as clusters of Si atoms cannot be justified - the image is a projection of a 200Å thick oxide, and random superposition of atoms from various specimen depths is known to produce seemingly non-random image features.[14] The absence of stationary features larger than the arrowed one however shows that inhomogeneities much larger than 5Å are not present in the oxide.

Average changes in the oxide composition should be reflected in its average scattering power, and this might give rise to broad contrast features such as dark or bright bands near the interface. However, our calculations show that the difference in elastic scattering of SiO and SiO_2 never exceeds 10% at any point in reciprocal space. Any such features would therefore be extremely faint. The dark band previously observed by us[15] in a tilted illumination image, obtained with a microscope of somewhat lower resolution than the one used here, is therefore almost certainly an artifact arising by a failure to achieve exact coincidence of the Bragg beams, and the same probably applies to another independent observation[16] of the "transition region" by EM.

CONCLUSIONS

We have shown that the transition from the Si crystal to the amorphous oxide happens quite abruptly (within about 3Å). One plane high atomic steps separated by 20-40Å occur on all the interfaces, and most interfaces also appear to show a long range modulation of 4-8Å height, and a wavelength of 200-500Å. Overall, the structure of the three types of interfaces examined here appears to be quite similar.

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FIGURE CAPTIONS

Fig. 1. a) Low magnification image of the finished cross-section through a (100) MOS. b) Electron diffraction pattern from the Si crystal.

Fig. 2. High magnification images of (100), (111) and (911) interfaces. The major planes in the Si crystal are indicated. The best way to see the steps on the Si crystal surface is to rotate the page by 90° and view it from a low angle.

Fig. 3. Images of 900Å long segments of (100), (111) and (911) interfaces. The departures from the reference markers show how the interface undulates. The Si crystal peaks are marked with arrows. The black line below the interface in the lower two images arises from the variation of the Si crystal's scattering with thickness (thickness fringe).

Fig. 4. A through-focal series of high magnification images of (911) interface. The arrowed feature does not disappear with a defocus change, but it is too small to be identified with a cluster of Si atoms.

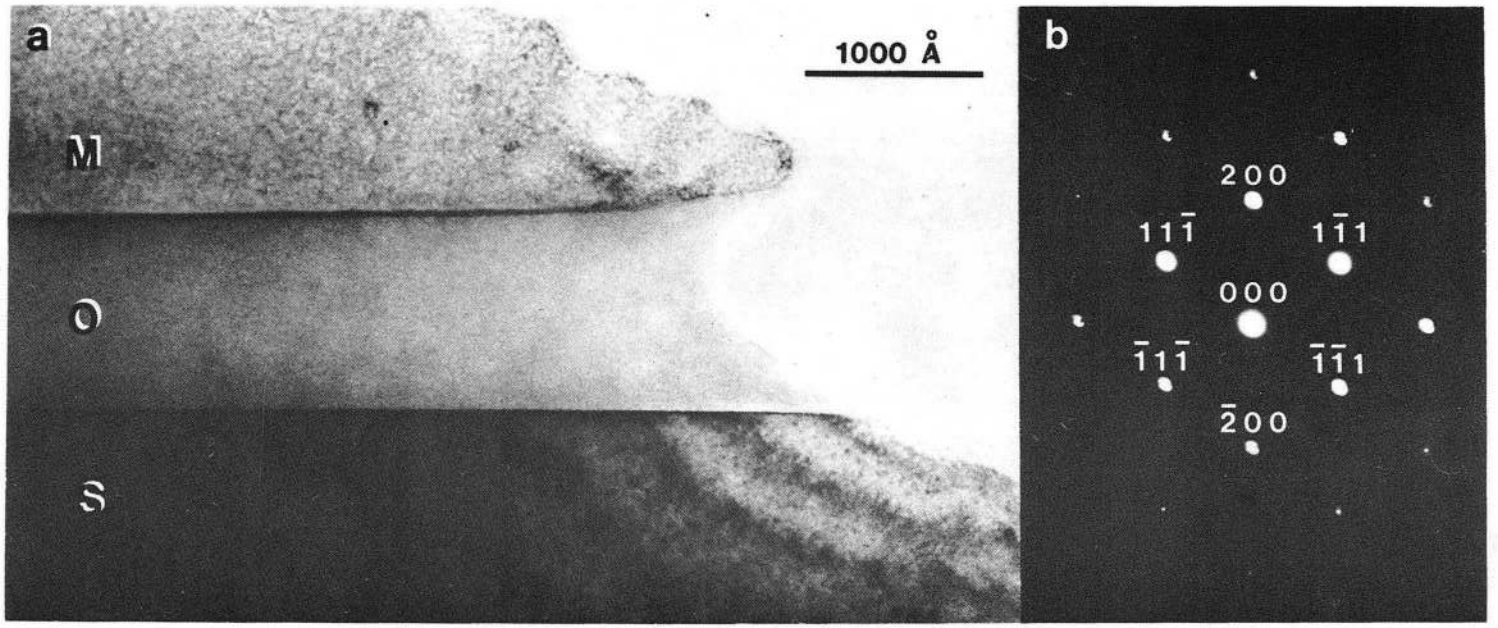

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Fig. 1.

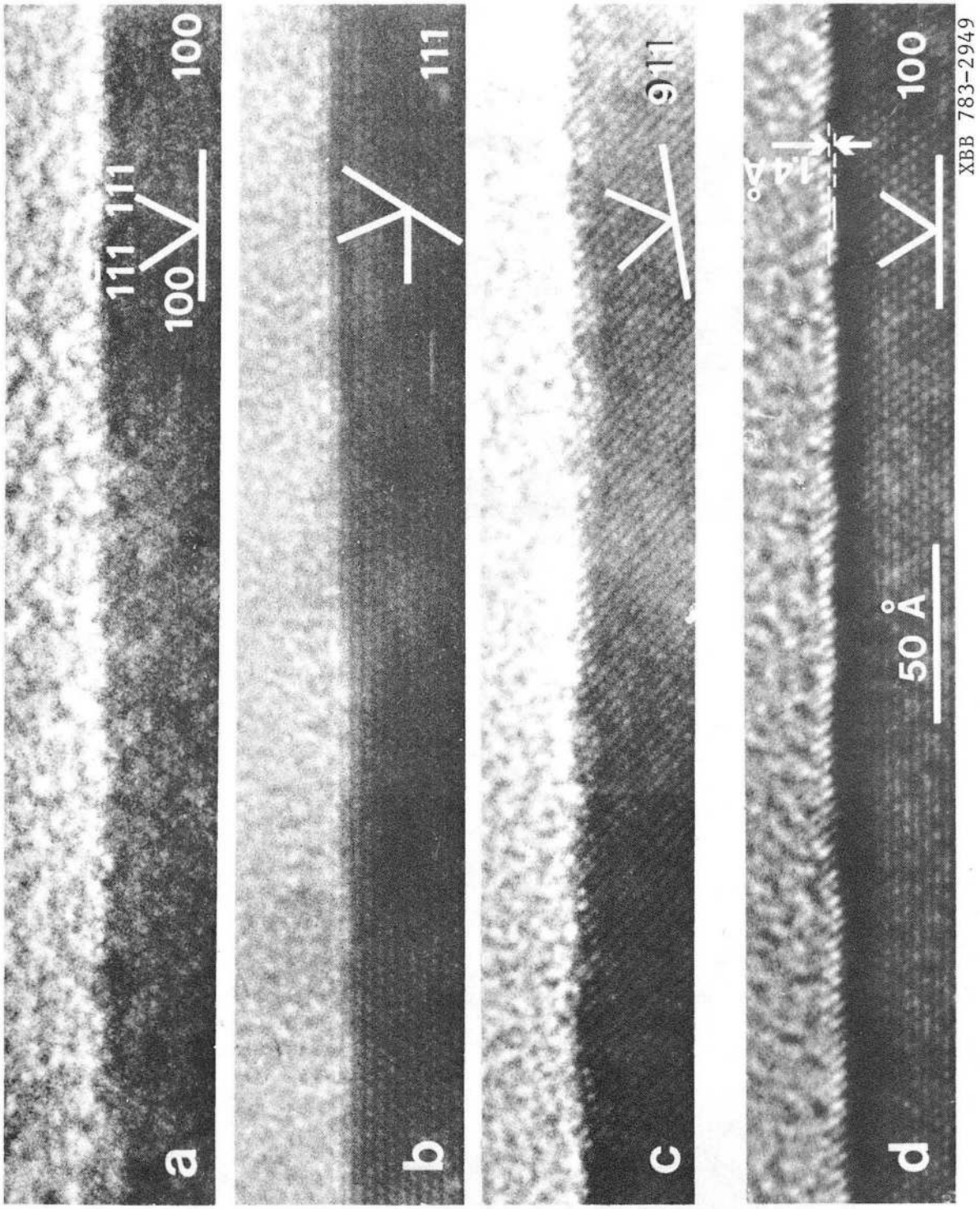

Fig. 2.

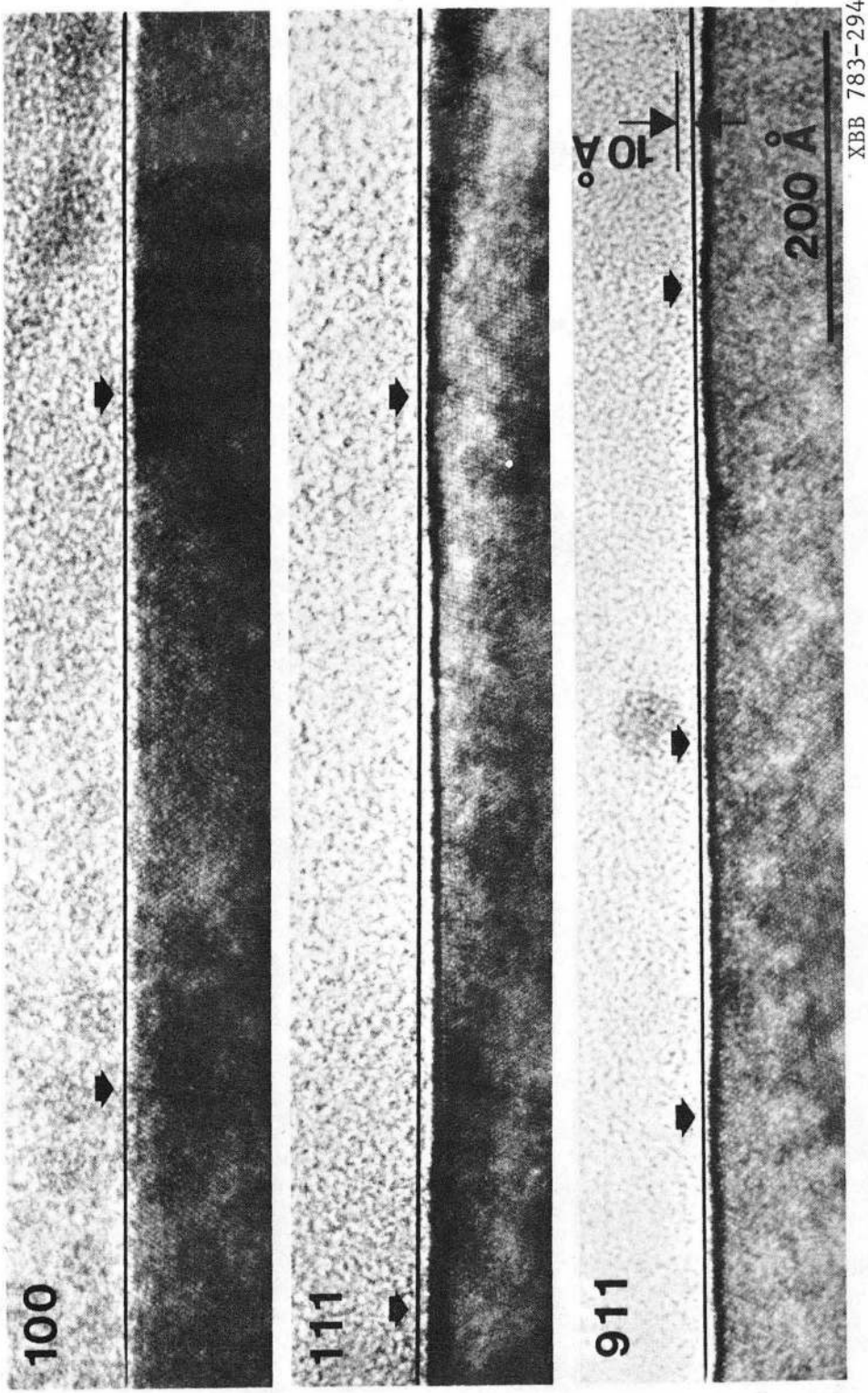

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Fig. 3

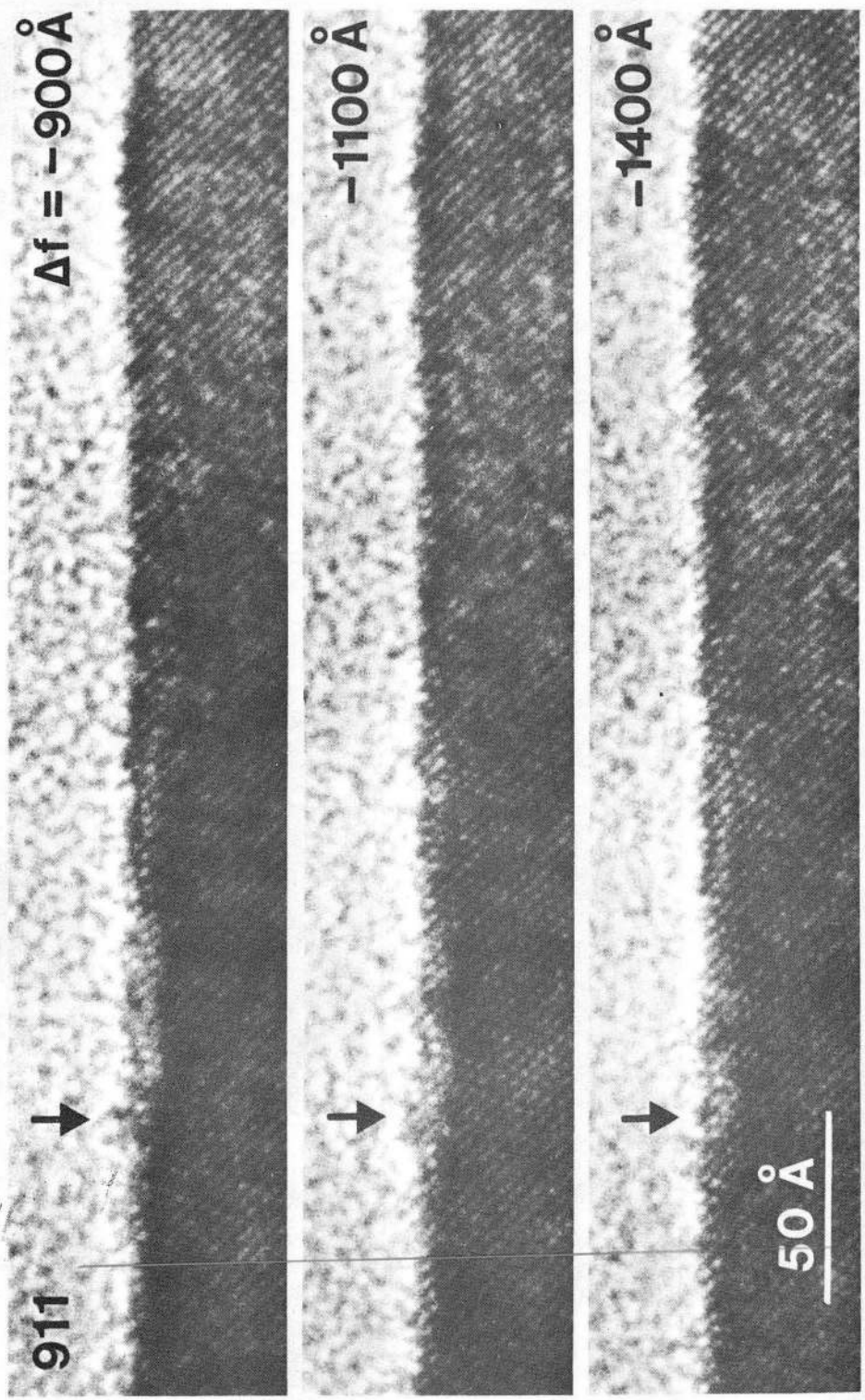

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Fig. 4.

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