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An Ordered Precipitate Structure and the Formation of Coesite in Oxygen Implanted Silicon

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The microstructure of high-dose oxygen implanted silicon was studied. In the silicon film above the buried oxide we observed a 5nm period superlattice of oxide precipitates 2nm in diameter. Below the oxide the silica phase coesite was found. The morphology of the oxide/silicon interfaces indicates that a locally reduced oxidation rate occurs at the lower interface. These observations are interpreted in terms of the anisotropic elasticity of silicon and point defect concentrations.

1. Introduction

Buried oxide layers can be formed by high dose implantation of oxygen in silicon. The resulting Silicon On Insulator (SOI) has interesting properties for device applications. The microstructure of this material depends sensitively on dose rate and temperature /1/. Elevated temperatures of about 500°C are required to retain the crystallinity of the silicon overlayer /2/. Subsequent anneals at very high temperatures of about 1300°C have produced silicon overlayers denuded of oxide precipiates with sharp silicon/oxide interfaces /2,3/. Here we report on a Transmission Electron Microscopy (TEM) study of the microstructure of as implanted wafers. This structure, we believe, is of great importance for the final result, even after prolonged annealing.

2. Experimental

Oxygen was implanted at an energy of 300 keV (using 600 keV O_2^+ ions) to a dose of $2.5\times10^{18}/cm^2$ into a circular region, 50 mm in diameter, of a 100 mm (001)-Si wafer (FZ, p-type, 20 Ωcm). The ion flux was about 1.5 $\mu A/cm^2$. The wafer was heated from the rear side by seven 250 Watt halogen lamps to a temperature of 500°C as measured by a thermocouple on the wafer. During the implantation the temperature increased to 550°C due to additional heating by the ion beam.

Cross-sectional specimens for TEM observation, being oriented near a [110] pole, were prepared by argon ion milling. Specimens in plan-view, i.e. along [001], were made by jet etching from the rear side using HF/HNO3 mixtures.

3. Results and discussion.

The complete structure consists of a 500 nm thick monocrystalline silicon layer on top of a 350 nm thick buried oxide. The microstructure of the superficial silicon film (fig.1) varies from top to bottom, which may be attributed to the increasing oxygen concentration. We distinguish three regions: Near the surface there is a region of dislocation free silicon, followed by a region again dislocation-free, wich contains a laminar structure. Close to the oxide we found dislocations at a fairly high density. The laminar structure extends laterally throughout the implanted area. The occurrence of a similar structure has been reported before /1,3/. It seems to require stable implantation conditions since variation of the beam current in the course of the implantation under otherwise similar conditions gave dislocation tanglements instead.

The laminar structure observed along the silicon [110]-zone axis, gives rise to additional diffraction spots, also shown in fig.1, correspondig to a periodicity of 5 nm along the silicon [001]-direction. High resolution micrographs (fig.2) show that the laminar region contains individual oxygen precipitates, 2 nm in size, spherically shaped, and embedded in a monocrystalline matrix. The size of the precipitates is constant throughout the entire thickness of the laminar structure. Since it has been shown that this type of oxygen is bonded to silicon /4/, it should concern oxide.

Examinations along the [010]-zone axis revealed a two-dimensional precipitate lattice, shown in fig.3. The coherency of the precipitate lattice is at least 50 nm, sufficient to give rise to additional diffraction spots instead of streaks, but only to the first order. Again, the periodicity is 5 nm, aligned along the two silicon [100]-directions. The plane view micrograph of fig.4 shows that the ordered structure can also be distinguished perpendicular to the surface. Altogether it appears that the precipitate network is oriented along the principal axis of the silicon lattice and has simple cubic symmetry with a lattice constant of 5 nm.

Ordering of voids and bubbles is known to occur in metals after ion irradiation /5/. To our knowledge this is the first time that a similar phenomenon has been observed in silicon. One may expect that ordering, whenever it happens, will occur in the directions of the minimum elastic constant of the matrix, which are the <100>-directions. Consequently a simple cubic structure of the precipitate superlattice is most likely, in agreement with the observations.

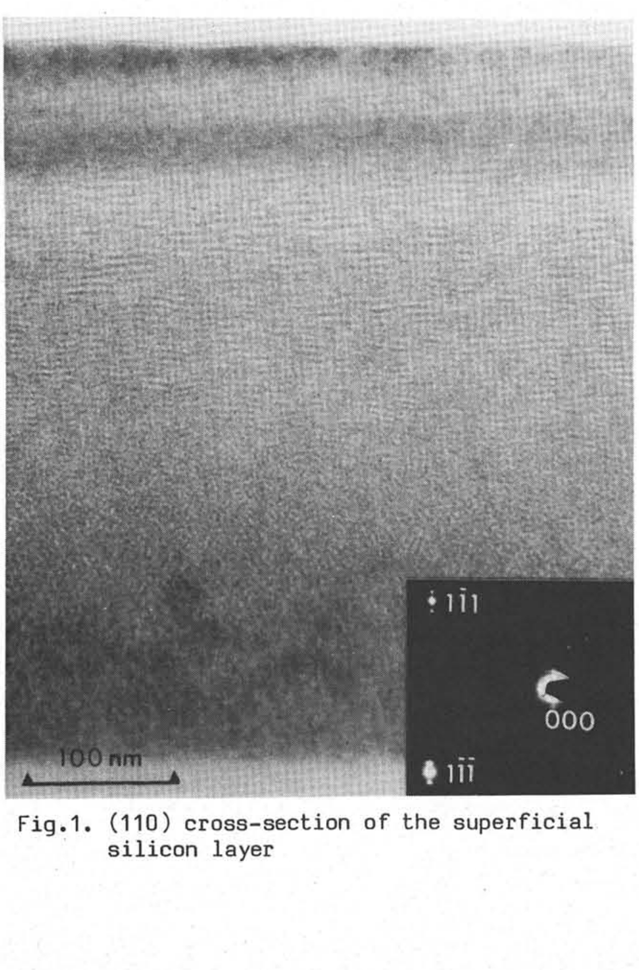

Fig.1. (110) cross-section of the superficial silicon layer

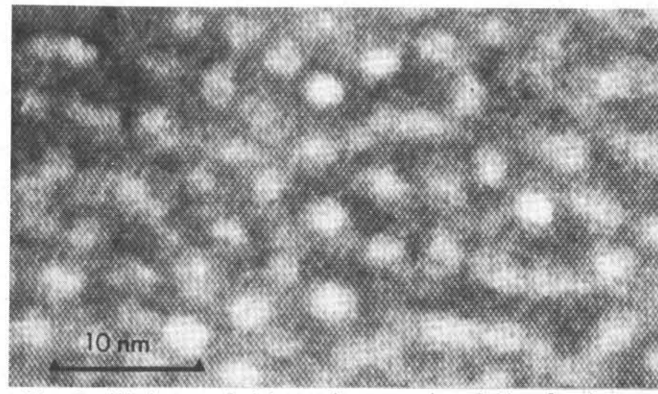

Fig.2. High resolution micrograph of the laminar region

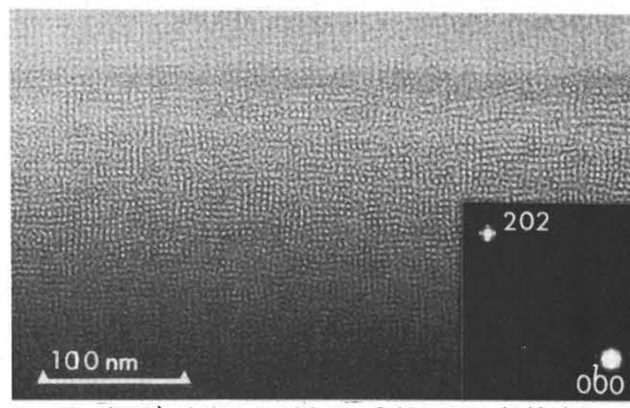

Fig.3. (010) cross-section of the precipitate superlattice

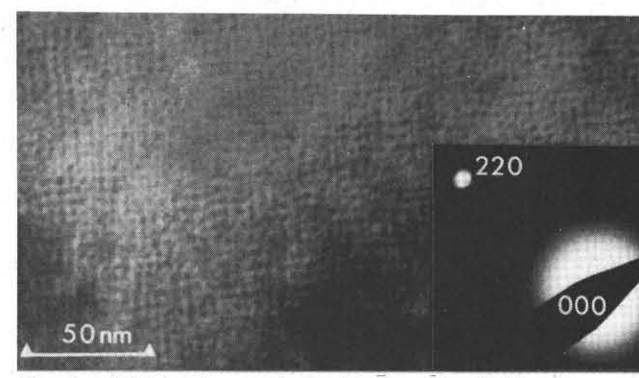

Fig.4. (001) plane view micrograph of the superficial silicon layer

We note an apparent difference between the upper and the lower interface of the buried oxide, the upper one being rather sharp and flat (fig.5) as compared to the meandering lower one (fig.6). Going down in fig.7, below the oxide, the precipitates are essentially of the same type as those above the buried oxide, but decreasing rapidly in size, corresponding with the steep decreasing oxygen concentration of the implanted distribution.

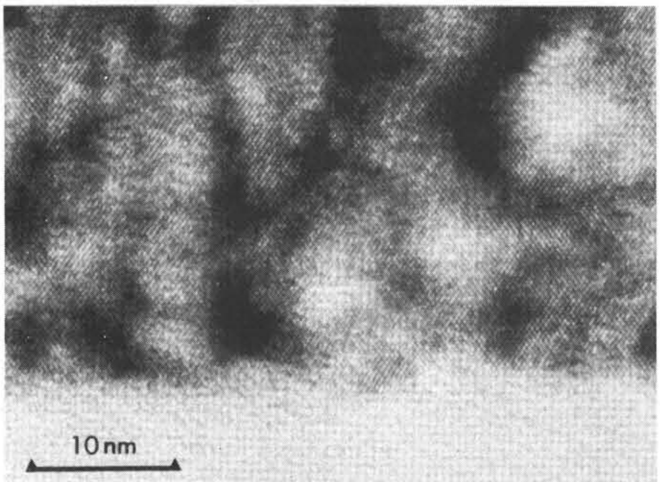

Fig.5. High resolution micrograph of the upper silicon/oxide interface

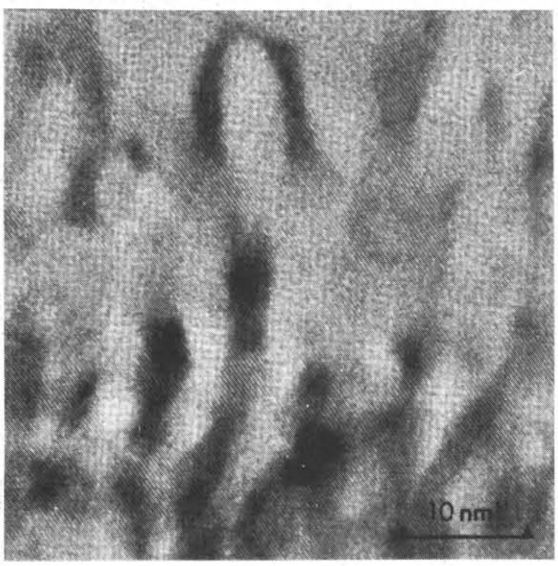

Fig.6. high resolution micrograph of the lower oxide/silicon interface

Underneath the amorphous precipitates, only plate-like precipitates occur, as can be seen in fig.8. The plates are crystalline and often change their habit plane from $(\bar{1}13)$ to $(1\bar{1}3)$. Occasionally (001) habit planes were observed as well. The interface with silicon (110)-planes is at least partially coherent. The thickness of the precipitates is only a few atomic layers (1nm), and their diameter is about 25 nm. In spite of the small thickness of the precipitates, subsidiary diffraction spots could be observed directly in the microscope after tilting of the specimen. An example is shown in fig.9, together with a dark-field image. The additional spots correspond to a lattice spacing of 0.31 nm along silicon [100].

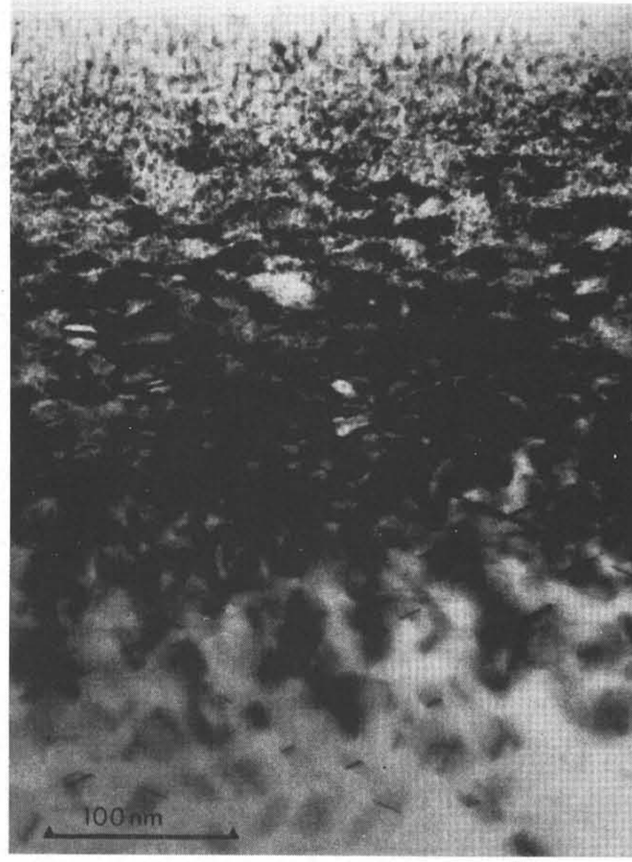

Fig.7. (110) cross-section of the silicon structure below the buried oxide

These observations strongly suggest that it concerns the monoclinic silica phase coesite, oriented with (010)coesite // (110) silicon. Coesite precipitates have also been observed in the bulk of Czochralski-grown silicon after heat treatments at temperatures of around 650°C /6,7/. In contrast with these observations we do not observe extended defects like dislocations and stacking faults, which generally occur in combination with coesite precipitates in the bulk of silicon.

During the implantation there is a continuous generation of both vacancies and interstitials. Due to the higher mobility of interstitials, an excess of vacancies may soon exist near the surface, possibly aggregated /8/, being perfect nucleation sites for oxide precipitation. This may account for a homogeneous distribution of precipitates, the possible precursor of the precipitate superlattice.

Once the buried oxide becomes a continuous film, however, the interstitials generated below this film can no longer reach the surface. Furthermore we did not observe any defects below the oxide at which interstitials could precipitate.

Fig.8. high resolution micrograph of plate-like coesite precipitates in silicon

Fig.9. dark field image and diffraction pattern close to the Si 221 -zone axis. The arrow indicates the (040)-coesite diffraction spot used for imaging.

Consequently, the interstitial concentration below the buried oxide is increased, reducing the oxidation rate. This accounts for the observation that the lower interface is rough, exhibiting the morphology of an oxide film which has just become continuous.

The formation of coesite may also be related to an increased concentration of interstitials, since it concerns the high pressure form of silica, which has a 40% higher density than amorphous SiO_2, and thus requires less strain relief.

4. Conclusions

Summarizing, we observed a 5 nm period superlattice of simple cubic symmetry consisting of 2 nm diameter oxide precipitates located above the buried oxide layer and oriented along the principal axis of the silicon matrix, in accordance with the elastic anisotropy of silicon. The occurrence of this superlattice is indicative of stable implantation conditions and replaces an otherwise observed tangled dislocation structure. The morphology of the lower interface of the buried oxide could be explained by a locally increased concentration of interstitials and a consequently reduced oxidation rate.

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