

was determined by a weighing technique to be approximately 2.9 g/cc. Silicon nitride was deposited on polished silicon wafers which had been previously weighed. The area covered by the nitride was measured and the average thickness measured. The wafers were reweighed and the density calculated. The wafers were etched clean of silicon nitride and reweighed to verify the previous reading.

Using the deposition systems described, limited studies have been conducted on MOS properties of silicon nitride on silicon. Our results indicated the surface state density, N_{ss} , to be in the order of $10^{12}/\text{cm}^2$ and the capability to consistently deposit films in the 300Å range. This is comparable to that reported by Chu *et al.* (7) and Doo *et al.* (8). However, we have not studied charge storage effects or other properties presently considered important for gate dielectrics.

Sodium Penetration Testing

A radioactive tracer technique (3) is used to test the effectiveness of silicon nitride as a barrier to sodium penetration. Radioactive sodium in the form of sodium chloride is evaporated onto the film in a vacuum, heated to 600°C for 22 hr, and diffusion allowed to take place. Using a scintillation detector, a count of the gamma radiation from the Na^{22} is obtained for the surface and following each etch step to develop a profile. If after 50Å have been removed only 8% of the original concentration remains, it is implied that the film is a reliable barrier against sodium. The films deposited in this system consistently pass this test. A less sophisticated method of evaluating silicon nitride is by actually subjecting devices to a sodium chloride solution (10g NaCl/100 ml H_2O) during a certain baking period of 300°C for 8 hr, and then testing the semiconductor devices for high leakage currents.

Conclusion

An operating high production system for the deposition of silicon nitride using the ammonolysis of silicon

tetrachloride has been described. The unit has the capability of at least 60 wafers/run.

From the data presented, it has been shown that the system has repeatability and reliability over a large number of runs with silicon nitride varying less than $\pm 250\text{Å}$ within the run. The assembly costs are relatively inexpensive, and the actual operation is quite simple and reliable.

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Dislocation Etch for (100) Planes in Silicon

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ABSTRACT

A new etch composed of a dilute aqueous solution of an alkali dichromate and hydrofluoric acid, for suitably revealing dislocations and other lattice defects in (100) planes of silicon, is reported. The etch is fast (typically 5 min), brings out both lineage (low angle grain boundaries) and slip lines, and works over a wide range of resistivities for n- and p-type material. The application of the etch is not restricted to (100) planes; dislocation etch pits are formed on all crystallographic orientations. The same etching characteristics were found with dilute aqueous solutions prepared from various chromium compounds and hydrofluoric acid.

The two etches primarily used to reveal dislocations in silicon are the Dash etch (1) and the Sirtl etch (2). The Dash etch yields deep etch pits on any surface independent of its crystallographic orientation. It has, however, the drawback of requiring long etching periods (4 to 16 hr) and is sensitive to oxygen impurity concentration.

The fast working Sirtl etch is almost exclusively used as a preferential etch for crystallographic defects in silicon but fails to produce pits on (100) planes and on planes close to (100) orientation [e.g., (115)]. Mounds are formed instead, resulting in a rough sur-

face and loss of detail. Using a modified Sirtl etch, a correlation between mounds and dislocations has been reported recently (3). However, the effectiveness of the etch is hindered due to the formation of numerous mounds of various sizes which do not appear to be related to dislocations.

In view of the previous difficulties, an effort was made to develop an improved dislocation etch for (100) planes of silicon. Such an etch should meet the following minimum requirements: (i) well-defined (deep) etch pits must be developed at the emergence points of all dislocations, including slip and lineage arrays; (ii) the etch must work for a wide range of resistivities and for n- and p-type material; (iii) the etch must

Key words: silicon crystals, etchants, dislocations, crystal imperfections.

work in a reasonably short time and be sensitive only to crystallographic defects (avoid surface roughness and formation of artifacts). An etch containing a dilute aqueous solution of an alkali dichromate and hydrofluoric acid was found which meets the above requirements. Moreover, the etch is isotropic in that it appears to reveal dislocations on surfaces of all orientations.

Experimental

Before etching, the silicon wafer is chemically polished. This step is important because a rough or dirty surface will automatically cause a poor etching. Any modification of the $\text{HNO}_3\text{-CH}_3\text{COOH-HF}$ polishing mixture leading to a shiny surface can be used. A commercial polishing solution of the composition $\text{HNO}_3/\text{CH}_3\text{COOH}/\text{HF}$ (3:2:2) was used in our experiments. After 2-3 min, the polishing solution is rapidly flushed away with water. Particular care should be taken not to touch the wafer with the fingers or gloves, as this can result in subsequent anomalous etching effects. The standard dislocation etch recommended consists of one part by volume of a 0.15 molar solution of $\text{K}_2\text{Cr}_2\text{O}_7$ in distilled H_2O and two parts HF (49%). The etchant was tested on (100) wafers cut from dislocated crystals of different resistivities and type. The resistivity range was from 0.01 to 10,000 ohm-cm. P-type (doped with boron) and n-type (P, As, Sb) crystals were examined.

An etching time of 20 min is necessary to bring out dislocation pits of a size suitable for counting purposes in crystals with resistivities between 1 and 10,000 ohm-cm. Agitation strongly reduces the etching time. By using ultrasonic agitation, it can be lowered to 5 min. Ultrasonic agitation also leads to an improved surface appearance, avoiding bubble formation, and is, therefore, recommended. Lower resistivity wafers require longer etching periods of the order of 10-15 min with agitation. After a few minutes of etching, the etch changes to a brown-green color. This is due to the formation of Cr^{3+} cations and does not seem to affect the strength of the solution significantly.

The bulk etching rate was determined from thickness measurements at etching intervals of 10 min for dislocated and dislocation-free wafers in the resistivity range 4-300 ohm-cm, p- and n-type. Thickness measurements were made with a precision micrometer on a circular zone of approximately 8 mm diam in the center of the wafer. The wafer was held vertically and the etch temperature was kept between 25° and 30°C.

Results

A dark field view of a (100) Czochralski wafer etched 5 min is shown in Fig. 1. Perpendicular slip lines, which are dense near the periphery and less pronounced toward the center, are visible. Figure 2 shows a (100) wafer cut from a float-zoned crystal of $\langle 111 \rangle$ orientation. The white irregular lines, mostly radiating from the center of the wafer, are lineage or low angle grain boundaries. A closer view of the etch pits forming slip and lineage is given in Fig. 3.

In order to demonstrate that each etch pit corresponds to a dislocation, an x-ray topograph of a (100) wafer was compared to an optical image of the etch pattern of the same wafer (Fig. 4a and b). Superimposing a magnified view of the topograph to the etch pattern resulted in Fig. 4c which shows that a one-to-one correspondence between etch pits and dislocations does exist.

The effect of the etch is not restricted to (100) planes. An optical micrograph showing the shape of the dislocation pits on four different planes is given in Fig. 5. The shape of the pits varies from elliptical to circular. This indicates a basically nonpreferential character of the etch. The pits exhibit shapes no longer dictated by crystal symmetry, as in the case of the Sirtl etch, but instead they develop a pattern due to the pursuit of defects down into the crystal. When the dislocation line is perpendicular to a certain crystallographic plane, a

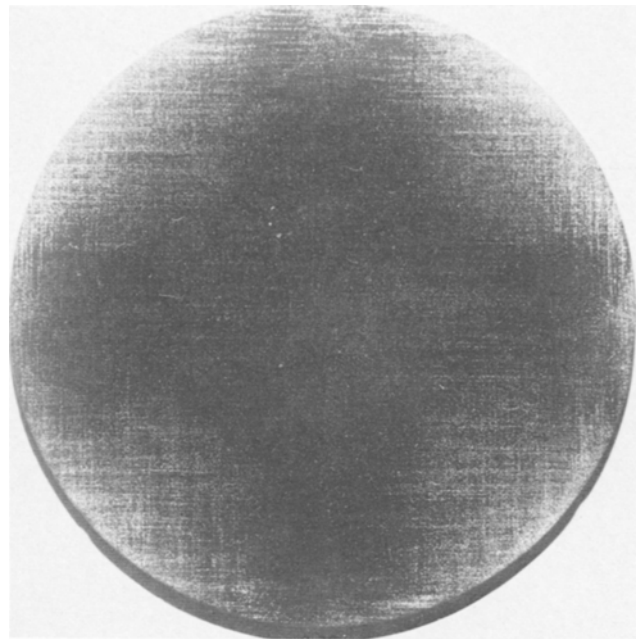


Fig. 1. Slip lines on a (100) Czochralski wafer, p-type (boron) with $\rho \approx 300$ ohm-cm; etching time, 5 min.

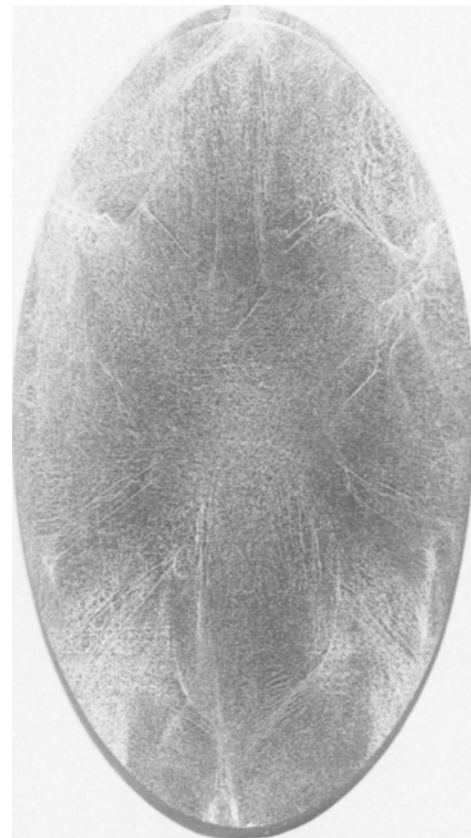


Fig. 2. Low angle grain boundaries (lineage) on a (100) wafer cut from a float zone crystal of $\langle 111 \rangle$ orientation, n-type (phosphorous) with $\rho \approx 1000$ ohm-cm; etching time, 5 min.

circular pit will form as a result of the symmetrical circular strain around the dislocation. As expected, more circular pits are present on (110) planes. These are probably due to dislocations aligned in the $\langle 110 \rangle$ direction meeting the surface under an angle of 90°. On the other planes, the orientation of the elliptical pits is mostly random and determined by the angle the dislocation line makes with the surface. Variation in

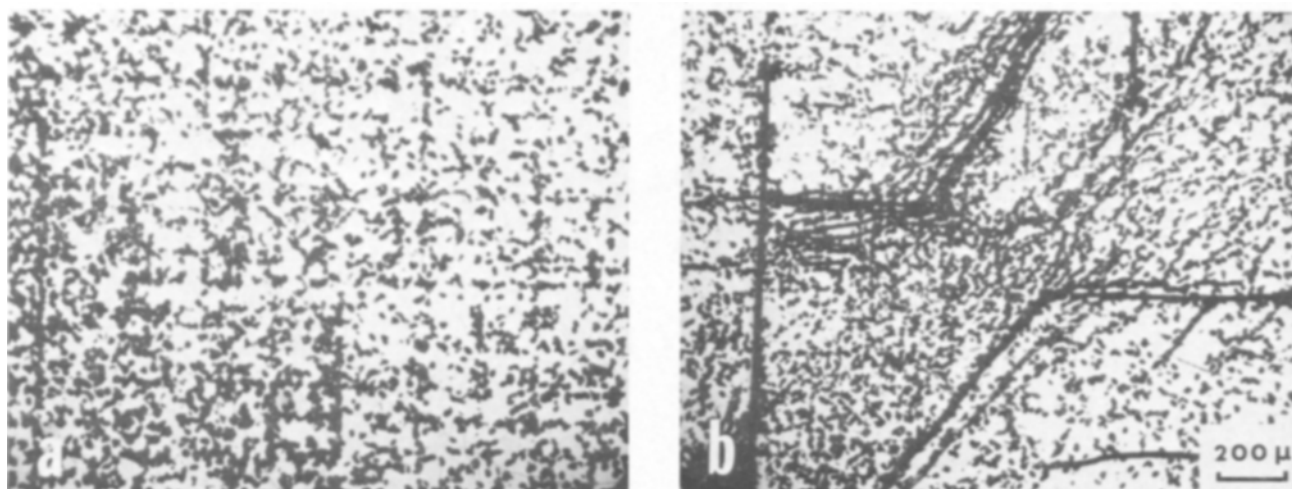


Fig. 3. Magnified view of the etch pits of the slip lines (a) and low angle grain boundaries (b)

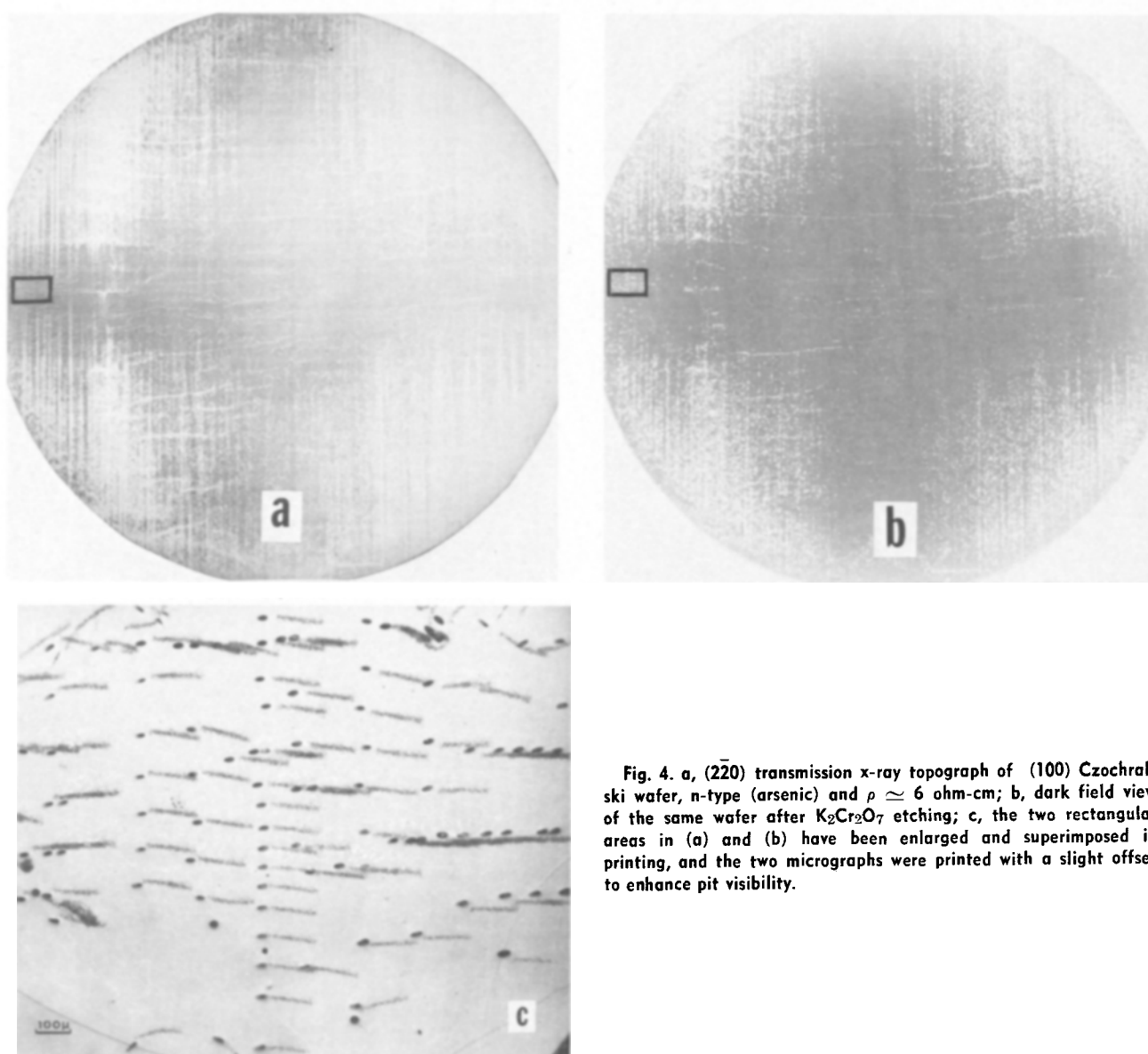


Fig. 4. a, (220) transmission x-ray topograph of (100) Czochralski wafer, n-type (arsenic) and $\rho \approx 6$ ohm-cm; b, dark field view of the same wafer after $K_2Cr_2O_7$ etching; c, the two rectangular areas in (a) and (b) have been enlarged and superimposed in printing, and the two micrographs were printed with a slight offset to enhance pit visibility.

pit shapes at dislocations in germanium, when the ratio of HF to HNO_3 is varied, was reported by Faust (4).

When dislocation-free crystals grown by the float zone method are usually etched, swirls of shallow triangular pits are usually seen on (111) planes. These pits are thought to be due to vacancy clusters (5) and

have been extensively described (6). Due to the non-preferential character of the dichromate etch, the same defects cause shallow circular pits and their shape does not vary with the orientation of the silicon slice.

A typical curve for the bulk etching rate of the standard mixture is represented in Fig. 6. The etching

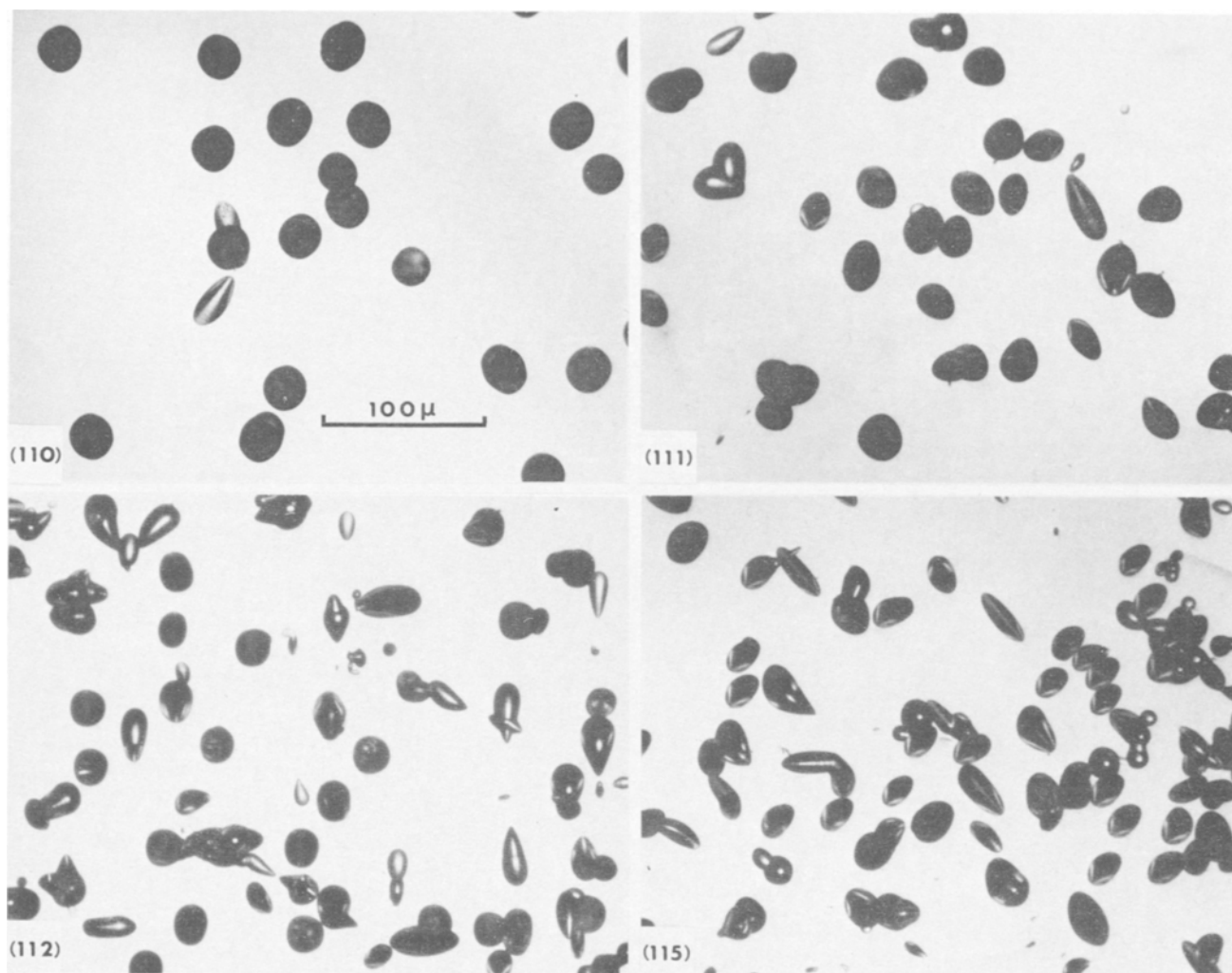


Fig. 5. Appearance of dislocation pits on (110), (111), (112), and (115) planes

rate is linear and equal to approximately $1.5 \mu/\text{min}$. No appreciable variation in etching rate exists between dislocated and dislocation-free crystals. Other lattice defects such as, for example, the hillocks of the swirl pattern (6), stacking faults, twin boundaries, etc., are also revealed by the etch.

The results reported above refer to a dilute (0.15M) aqueous solution of $\text{K}_2\text{Cr}_2\text{O}_7$ and HF. Etch pits with properties similar to those described may be formed also by using $\text{Na}_2\text{Cr}_2\text{O}_7$ as the oxidizing agent. At first it was thought that the presence of alkali ions in the recommended standard etch causes the better orientation-insensitive etching compared with the CrO_3 -HF

system. However, this concept was disproved when similar results were obtained substituting $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ or CrO_3 for the alkali dichromate. The main difference between the standard Sirtl etch and the etch described in this paper is a decrease in the content of Cr cations in the present etch accompanied by an increase in the acidity of the solution. These two factors together probably play the most important role in accounting for the different etching characteristics.

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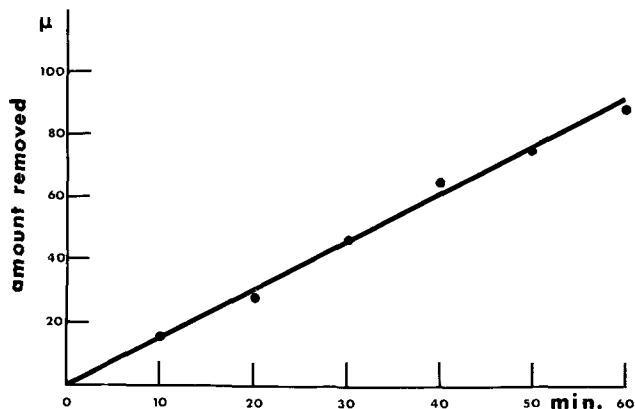


Fig. 6. Etching rate for the dichromate etch