Letters

Influence of impurity adsorption on the properties of silicon single crystal layers

The substrate surfaces used for growing epitaxial layers on them, are never ideal, their atomic structures are always contaminated by some unwanted radicals. These contaminations are due to the various chemical treatments in the production process and to the atmospheric effects during the storage of the components. In the case of silicon the free surface bonds of the substrate are saturated mostly by the radicals of some oxides, fluorides, nitrates, acetates, etc. Even the widely used *in situ* etching by HCl-gas or other gases, before the build up of the epitaxial layers, may cause surface contamination as the chemical agents utilized in the reaction and the products created by the etching process may be bonded on the surface.

Although several methods are known for studying surface imperfections few investigations have been concerned with impurity adsorption on silicon substrates. The results of these research efforts are summarized below. Due to the surface treatments used, different anions have been found on silicon substrates [1], chlorine, carbon and oxygen impurities in thin silicon epitaxial layers [2], traces of iron and nickel (ppb level) on intensively cleaned silicon substrates [3-5], different metallic precipitates [6-9] and carbon impurities in silicon single crystal epitaxial layers, have all been reported.

This contribution is based on experiments with antimony and arsenic-doped silicon single crystal substrates, treated by the usual chemo-mechanical surface finishing [10] and cleaning procedure and the *in situ* etching method.

On the substrates, epitaxial layers were grown by the $SiCl_4$ process. In the evaluation of the surface parameters, phase contrast microscopy, electron microprobe and the IR-spectroscopic method of Yoshioka and Takaganagi [1] were utilized.

For clarifying the adsorption phenomenon the

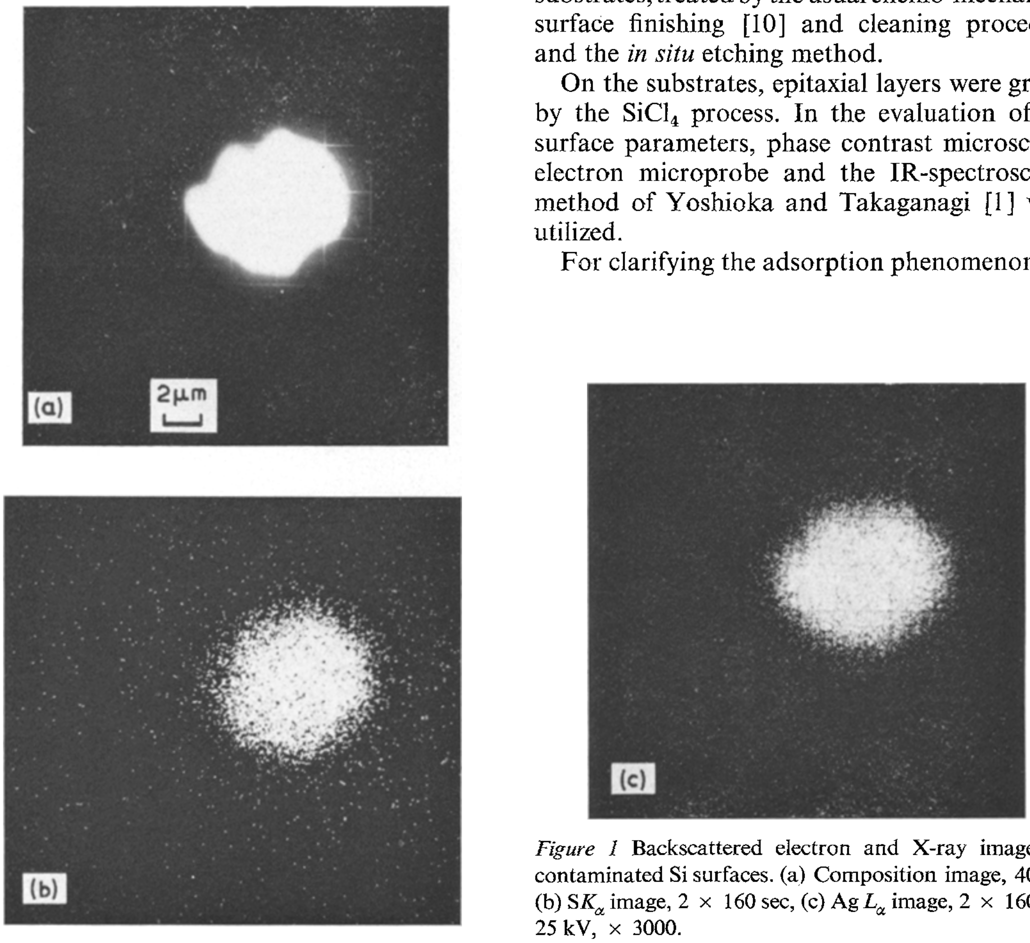

Figure 1 Backscattered electron and X-ray images of contaminated Si surfaces. (a) Composition image, 40 sec, (b) SK_α image, 2 × 160 sec, (c) Ag L_α image, 2 × 160 sec. 25 kV, × 3000.

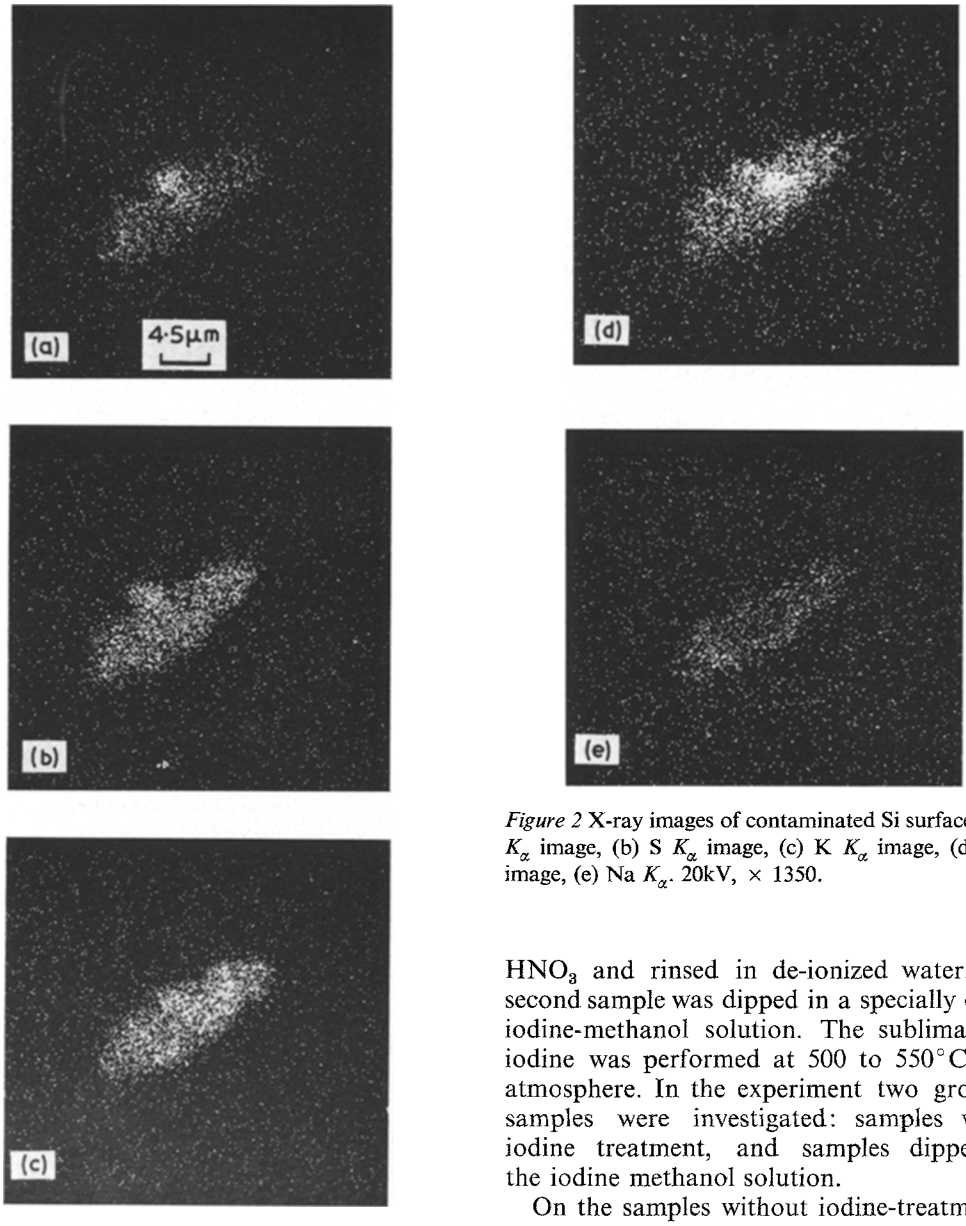

Figure 2 X-ray images of contaminated Si surfaces. (a) Cl K_α image, (b) S K_α image, (c) K K_α image, (d) Ca K_α image, (e) Na K_α. 20kV, × 1350.

exchange reaction between the originally adsorbed impurities and iodine ions was investigated, using a somewhat modified version of the iodine surface protection method proposed by Lieberman and Klein [11]. The single crystal silicon samples used in the experiments were first polished chemo-mechanically, then treated in hot A.R. CCl_4, cleaned ultrasonically in a detergent solution and in high purity deionized water, etched in a solution of A.R. HF. and A.R. HNO_3 and rinsed in de-ionized water. Every second sample was dipped in a specially cleaned iodine-methanol solution. The sublimation of iodine was performed at 500 to 550°C in H_2 atmosphere. In the experiment two groups of samples were investigated: samples without iodine treatment, and samples dipped into the iodine methanol solution.

On the samples without iodine-treatment the presence of Si-O, Si-F and Si-N bonds could be detected by means of IR-spectroscopy. In the same sample group, electron microprobe analysis has shown enrichment of some nonmetallic groups, primarily O, Cl and S. The enrichment of O, Cl and S impurities can lead to the formation of smaller (diameter: 1 to 5 μm), or larger (diameter: 15 to 35 μm) hillock-like inclusions. These inclusions could be detected on the substrate surface and on the surface of the silicon single crystal epitaxial layers, if there were unwanted metallic impurities in the environment.

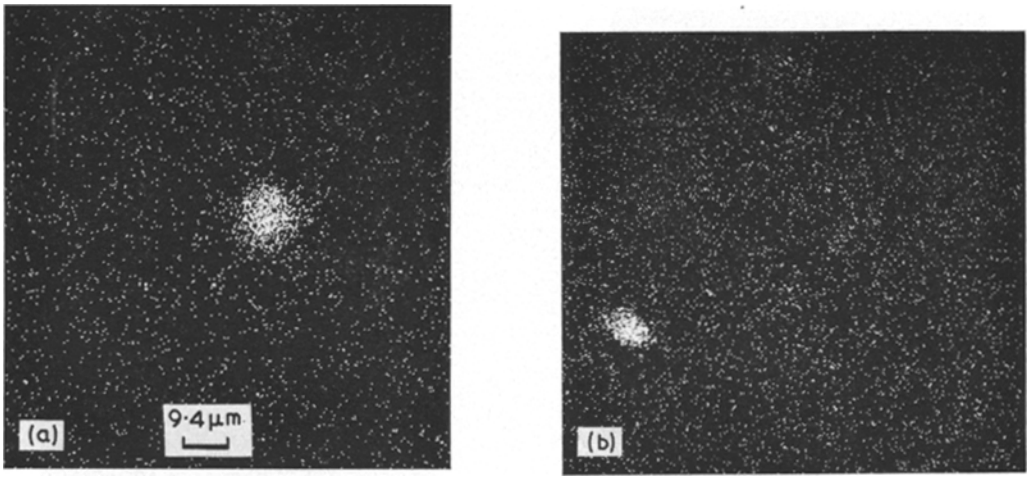

Figure 3 X-ray images of iodine treated Si surfaces. (a) and (b) I L_α images. 20 kV, × 643.

In the case of metallic impurities further observations could be made as follows: S-enrichment was accompanied by Ag-codeposition (Fig. 1). The common enrichment of O, Cl and S induced the codeposition of Ca, K and Na (Fig. 2), but rarely that of Mg or Ba impurities.

Previous experiments using a new emission spectroscopic method of high sensitivity [9-12], have already detected Ag and Ca traces in epitaxial layers containing the mentioned hillock-like precipitates.

It has also been proved by previous workers that these impurity precipitates decrease the breakdown voltage of silicon diodes [13].

In the second group of samples treated by iodine we found, however, iodine enrichment and adsorption only (Fig. 3). These observations can be taken as a direct proof of the assumption of Lieberman and Klein [11], containing the exchange of different adsorbed anions and iodine on the single crystal silicon surface. After 48 h of storage the iodine could still be detected on the samples, due to the chemical nature of the adsorption.

The investigations described above were repeated with silicon substrates having dislocation densities from 10^3 to $10^5/\mathrm{cm}^2$, giving the same results. This proved that the dislocation density does not influence, significantly, the iodine adsorption and the exchange reaction with the non-metallic groups.

The codeposition of different impurities during the growth of single crystal Si-epitaxial layers is governed by special and not well understood equilibrium conditions. Our results indicate that some of the adsorbed impurities, especially O, Cl and S, enrich together on the surfaces of silicon wafers as a result of the different surface finishing and cleaning procedures. If traces of metallic impurities are present in the environment, this enrichment leads to defects, mostly in the form of unwanted inclusions or precipitates. By a suitable iodine treatment, however, the formation of these precipitates can be greatly limited since there exists an exchange reaction between the adsorbed impurities and the iodine agent.

The influence of F^- or NO_3^- adsorption on the formation of metallic impurity inclusions has not been determined.

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Direct observation of magnetic domain structure in plated-wire memory devices

Manufacture of computer memory store elements from plated-wire devices is now an established procedure. Typically 2500 Å of permalloy is electrodeposited on a thin (0.005 in.) copper-beryllium wire which carries a current to ensure a circumferential easy axis in the coating. Subsequent annealing reduces the magnetostriction to close to zero protecting the device from the effects of accidental stress [1]. In order to determine the coercive force and other magnetic properties of the permalloy it is necessary to control carefully the nature of the surface onto which electroplating occurs, the conditions of electrodeposition and the annealing treatment. The absence of a routine method of studying domain and ripple structures of electrodeposited films has complicated the search for optimum conditions of production. As surface observations are severely hampered by the necessary roughness of the permalloy coat [2] we decided to work in transmission with an electron microscope. In view of the thickness of the permalloy it was necessary to use a high voltage microscope [3] and our observations were made at 1 MeV.

We first established the specimen position and degree of objective lens excitation for the Hitachi microscope at the Berkeley Nuclear Laboratories so that the domain structure was preserved in the permalloy (coercive force 10 Oe). Specimens were prepared by cutting at 45° to the wire axis with the fine range of a spark cutting machine. The copper beryllium core was removed to a distance of 0.3 mm from the cut, by complexing with ammonia, this distance being chosen to facilitate electron microscope examination with the minimum possible disturbance of the memory element. The resulting "pen quill" specimen is shown in a scanning micrograph (Fig. 1). Note the rough circumferential line of contrast demarking the limit of removal of the copper beryllium (the contrast is the reverse of what we had expected).

Once prepared, specimens were glued to the edge of a 3 mm diameter ring with the "pen quill"

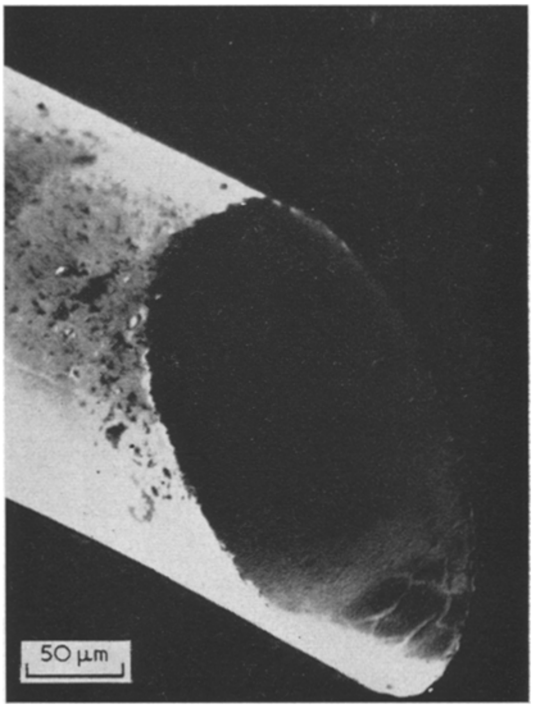

Figure 1 Pen quill specimen ready for transmission electron microscopy. The darker region visible at the top left hand corner of the wire shows the presence of underlying copper beryllium.