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A RHEED study of *as-received* and atomically clean Silicon surfaces in UHV-environment

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Surface reconstruction of {111}- and {100}- oriented silicon is studied. Decontamination by *ex situ* chemical processes and *in situ* thermal treatment is a key requirement for a controlled reconstruction to be observed. Only after a high temperature annealing at 1200 °C for several minutes was the (7x7) and (2x1) reconstruction obtained, which we explain by SiC desorption. Once generated the reconstruction stays stable for a long time even at increased gas pressure in the UHV-chamber.

1. Introduction

Advancement of silicon molecular beam epitaxy (Si-MBE) to production status depends in a large measure on basic materials problems relating to extended defects and contamination. Their reduction to tolerable levels as required for example in ULSI applications is of prime importance [1]. One of the essential steps to eliminate the problem of defects consists in obtaining an atomically clean wafer surface prior to deposition. Reflection high electron energy diffraction (RHEED) allows direct measurement of the surface structure of the substrate wafer and the growing epitaxial layer, even in a dynamic mode [see e.g. 2]. In the conditions which are usually employed in MBE, a collimated beam of energetic electrons in the range of 10…50 keV is directed at a low angle of 1…3° to the surface.

As the DeBroglie wavelength of this electrons is only a fraction of an Angstrom, diffraction pattern of the outermost arranged atoms are produced and displayed on a luminescent screen.

As-received silicon wafers exhibit surface contamination of many kinds. Usually an *ex situ* chemical cleaning process is applied in order to get rid of most of these impurities. Often a thin protective oxide is formed on the chemically cleaned surface, in order to avoid the adherence of contaminants during the transport in air of the wafers to the vacuum chamber (Shiraki clean [3]).

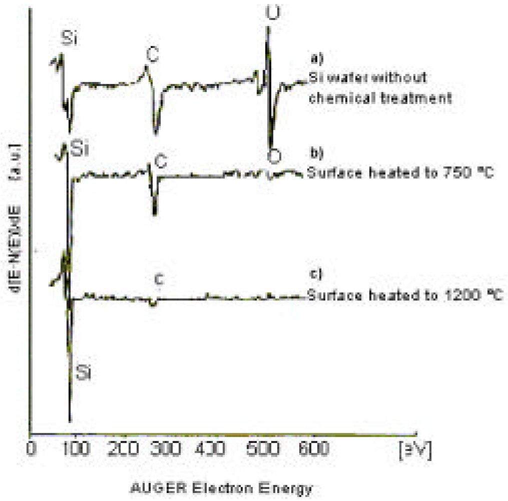

Fig. 1: AES of a silicon surface: (a) as-received wafer, (b) after a thermal annealing step in vacuum at 750 °C, and (c) at 1200 °C. The disappearance of oxygen from SiO_2 and carbon from SiC is clearly visible.

Special care has to be taken in the avoidance of carbide forming carbon. SiC is readily formed on a clean Si-surface, but due to its strong bonding, a desorption process at a relatively high temperature is needed. In the course of the present work, we found SiC as an important contaminant on the silicon surface, proven by Auger electron spectroscopy (AES), shown in Fig. 1. A temperature step as high as 1200 ° was applied in order to disrupt the Si-C bonding and to desorbe the carbon from the silicon surface. In this paper the generation of surface reconstruction of Si{111} and Si{100} in dependence on the annealing temperature of the wafer, and residual gas pressure in the UHV-chamber is described.

2. Experimental details and results

Czochralski-grown silicon wafers with a slight mis-orientation are used in this study. Almost contamination-free surfaces are produced by the following cleaning procedure: At first wafers were degreased in methyl alcohol and by boiling in trichlor ethylene for 15 minutes, followed by a boiling in HNO_3 at 130 °C in order to form a thin oxide layer which is removed by dipping into a 2.5% HF solution for 10 s.
Then the samples were boiled in a solution of HCl : H_2O_2 : H_2O (3 : 1 : 1) at 90 °C for 10 min to form a very thin protective oxide layer on the Si surface.

An uv/ozone procedure described elsewhere [4], was applied alternatively. After this procedure the samples were mounted on the substrates holder made of tantalum, which allows us to heat the sample by a direct current flow.

The wafer temperature during the annealing was measured by a Ni-NiCr thermocouple, which was placed close to the hot substrate surface, as well as by a pyrometer. The error in the absolute temperature measure was evaluated to 10 K, while relative temperature changes of 1 K could be detected with ease. At 900 °C the SiO_2 layer desorbes within a few minutes, but 1200 °C are needed to decompose SiC particulates. The figures 2a though f shows RHEED diagrams, which were obtained from surfaces of {111}-oriented Si in the

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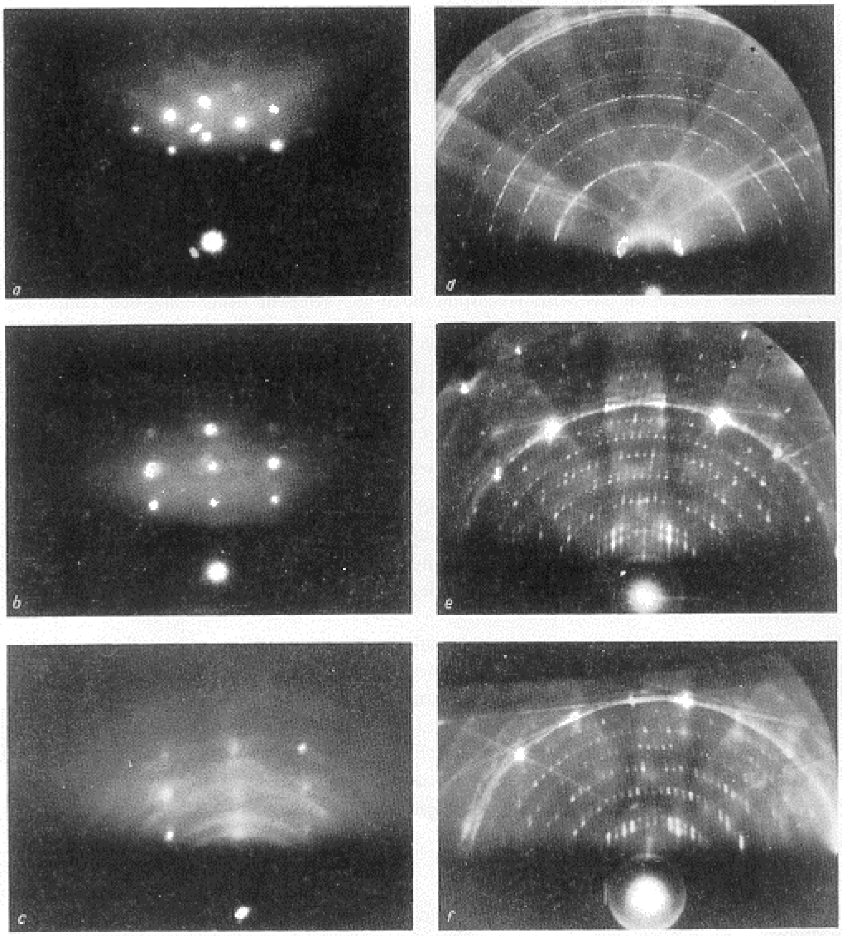


Fig. 2 (a through f): RHEED pattern obtained from {111} -oriented Si surfaces. (a, b): azimuth <110>, <211>; annealed at 700 °C for 5 minutes. Base pressure in vacuum chamber is $p = 7{\cdot}10^{-7}$ Pa. (c): azimuth <211> ; annealed at 850 °C for 1 hour. (d, e): azimuth <110>, <211>; annealed at 1200 °C for 15 minutes. (f): same sample after 50 hours at $p = 10^{5}$ Pa.

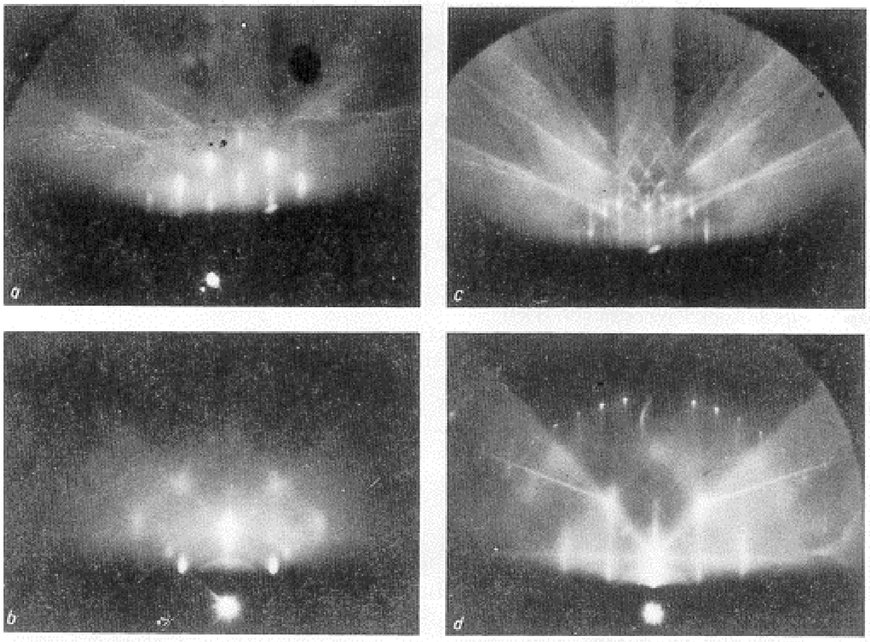
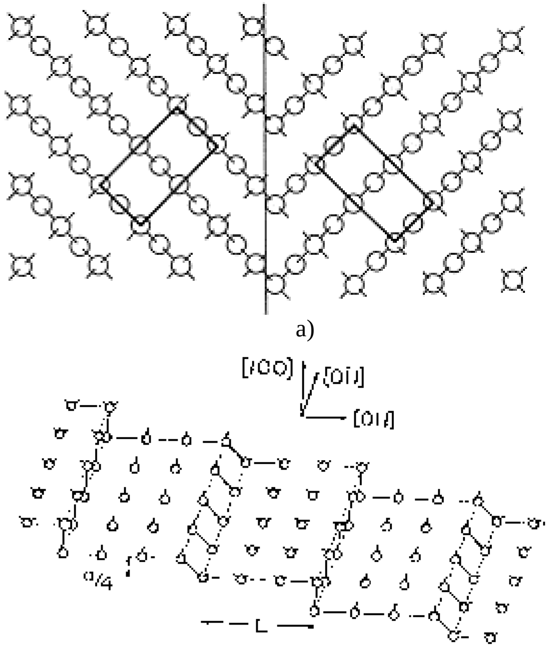


Fig. 3 (a through d): RHEED pattern obtained from a {100} -oriented Si surface. (a, b): azimuth <110>, <100>; annealed at 1200 °C for 10 minutes.


a)

b)

Fig. 4: Orientation of the unit meshes for a (2x1) reconstruction of a two-domain surface (a), containing a monoatomic step of a quarter lattice constant (b).

azimuths <110> and <211>, respectively. The dots in fig. 2a, b are representative of the bulk (or three-dimensional) diffraction of a rough surface. Polycrystalline surface deposits are seen via the rings in the RHEED pattern of fig. 2c at an increased annealing temperature, possibly due to the formation of SiC. The (7x7) reconstruction of the surface, representative of a chemically clean and geometrically perfect {111}Si-surface, is achieved only after heating to 1200 °C for about 15 minutes. The desorption of C at this temperature was already seen in the AES spectra of fig. 1. Many spots appears in fig. 2d, e arranged on rings around the primary reflection between the cero and the first order Laue zone indicating that the lattice mesh on the {111}Si surface is by a factor of (7x7) bigger than that of the bulk Si crystal.

The RHEED pattern of a {111}Si surface is shown in fig. 3. An annealing step of 900 °C for 90 minutes allows to obtain the pattern of fig. 3a, b, where additional spots in b suggest the formation of epitaxial SiC. Epitaxial growth of SiC on Si was previously described by INO [5]. A high temperature annealing step at 1200 °C for 10 minutes produced a pronounced surface reconstruction as shown in fig. 3c, d.

Here we find, that the substrate surface is characterized by a (2x1) unit mesh, but the diffraction spots arise from two orthogonal directions, seen in fig. 3d. Such a two-domain {100} - (2x1) structure is easily concluded from fig. 4: (2x1) domains are rotated by 90° against each other, which is possible, if the {100} surface contains monoatomic steps. Indeed, if a monoatomic layer is removed from a smooth {100}Si surface (a_0/4 - step), the direction of the bond chains are changed by 90°, and consequently the direction of the unit meshes as shown in fig. 4.

3. Conclusions

The reconstruction pattern of silicon-surfaces are observed by RHEED only after a high temperature step of 1200 °C. This finding is characteristic of the existence of carbon as SiC on the sample surface.

On the other hand, the reconstructed surface once established stays stable for a long time even if the residual gas pressure in the chamber reaches values of 10^{-5} Pa.

References

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