

## Invited

### Silicon Molecular Beam Epitaxy

Yasuhiro SHIRAKI

Central Research Laboratory, Hitachi, Ltd.

Kokubunji-shi Tokyo 185, Japan

Silicon molecular beam epitaxy (Si-MBE) has been demonstrated to achieve low temperature crystal growth, precise doping control and high quality silicide and insulator heteroepitaxy. New type multistructures of silicon/silicide and silicon/insulator can be formed, and doping superlattices can be easily fabricated by shutter operation of the dopant effusion cells thanks to low epitaxial temperature. These facts show the potential of MBE in realizing high speed, three dimensional and other novel devices. In this paper, various aspects of Si-MBE feasibility and applications are discussed.

#### 1. Introduction

The feasibility of a silicon molecular beam epitaxy (Si-MBE) technique has been carefully investigated and high-quality epitaxial films have already been grown using this technique. Consequently researchers are now exploiting Si-MBE in a variety of semiconductor devices. With LSIs and high-frequency devices, there has always been a strong demand for technologies which allow precise control of crystal growth, impurity doping, thin film and interface formations for multi-layer structures. MBE has the potential to respond to this demand, and to permit the fabrication of new, more sophisticated devices. Recently, there have been many attempts to perform not only silicon homoepitaxy but also a variety of film formation such as silicon on insulator, silicide growth, and poly-crystalline silicon deposition on non-crystalline substrates. In this review, the current state of silicon MBE and future prospects will be discussed.

#### 2. Homoepitaxy and Doping

Preparation of atomically clean surfaces is essential in order to achieve good epitaxial growth of silicon layers. Recently, it has been shown that low temperature ( $<800^{\circ}\text{C}$ ) thermal treatment is sufficient to eliminate contaminants on Si substrates<sup>1)</sup>. The temperature required to desorb protection oxide films was found to have

crystalline orientation dependence. In the case of (111) surfaces, the minimum temperature is around  $710^{\circ}\text{C}$ , but temperatures several dozen degrees higher than that for (111) are necessary for (100) surfaces. This might reflect the fact that since the (111) surface has one dangling bond on the surface while the (100) has two, the bonding strength is different.

A particular advantage of MBE is that it permits crystal growth at temperatures lower than conventional techniques such as CVD. In realistic MBE systems, the minimum temperature is around  $140^{\circ}\text{C}$ <sup>2)</sup>. This temperature is strikingly low compared with that for conventional methods. To date, however, device quality layers have been grown at temperatures higher than  $450^{\circ}\text{C}$ , which are nevertheless quite low and where thermal diffusion can be ignored.

Evaporation doping is a commonly used method and can be conducted by controlling the partial pressure or varying the substrate temperature. The fact that the sticking probability strongly depends upon substrate temperature is characteristic for evaporation doping, though it complicates MBE growth.<sup>3)</sup>

Abrupt change of dopants can also be accomplished by operating shutters located in front of the dopant cells. The doping superlattice structure shown in Fig.1 was created by sequential operation of both shutters for Ga

and Sb dopants. Periodic changes in impurity concentration are seen but unavoidable smearing of the SIMS measurement covers the real impurity profile, although the transition region is less than  $100 \text{ \AA}$ .

The drift mobility of the Si-MBE layers at room temperature is shown as a function of impurity concentration in Fig.2. As seen in this figure, the Sb-doped MBE layer mobility is comparable to that for bulk crystals (the solid line in the figure). However, Ga doped layers are inferior to bulk crystals and doping efficiency is low. There might exist unactivated Ga impurities causing lattice defects. The upper limit of MBE doping levels appears to be less than dopant solubilities, and  $1.4 \times 10^{18} \text{ cm}^{-3}$  for both n- and p-type layers.

Ionization doping is a very promising way to overcome these evaporation drawbacks. Doping level can easily be controlled with measurement of the ion beam current. The sticking probabilities increase and are nearly one. Moreover, the highest doping level for Sb increases up to an order of  $10^{20} \text{ cm}^{-3}$ , which seems to exceed the solubility limit<sup>3)</sup>. The ionization doping does not seem to cause the crystallographic or electronic qualities of the films to degrade. Therefore, it will become an essential technique if Si MBE is to be practically used for device fabrication.

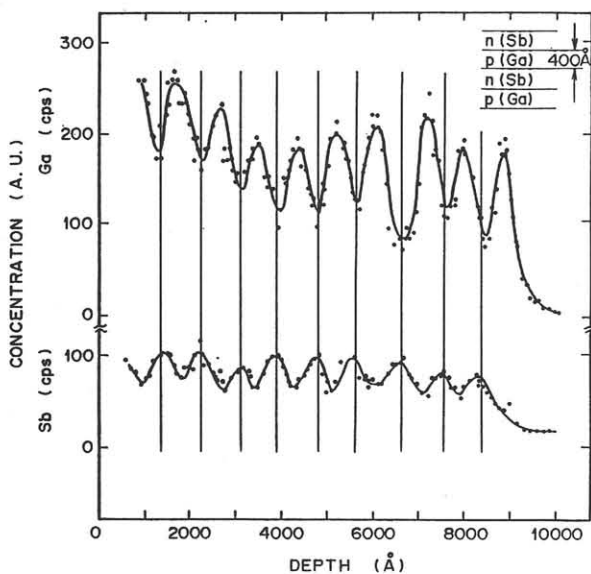


Fig. 1 Impurity profiles measured by SIMS in Si doping superlattices.

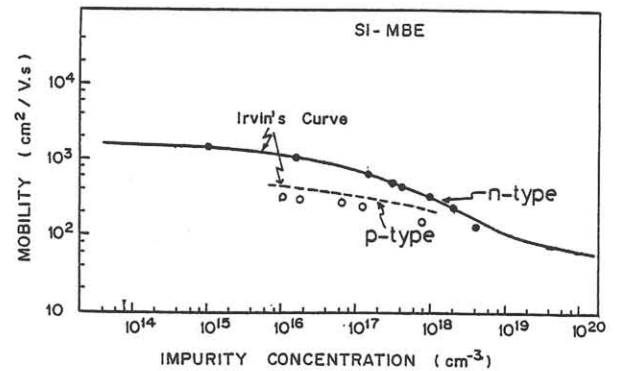


Fig. 2 Electron mobility of Si MBE layers as a function of impurity concentration.

### 3. Heteroepitaxy

Heteroepitaxy potentially can extend the capabilities of semiconductors as electronic materials and lead to new devices. In the Si MBE field, there are also interesting heteroepitaxies, that is, metal/semiconductor and insulator/semiconductor multistuctures.

Epitaxial silicide films formed on Si substrates are particularly attractive for use not only for forming contacts but also in fabricating novel devices. High quality epitaxial growth of silicides has recently been exploited by using Si MBE techniques. Tung and his coworkers<sup>4)</sup> have reported that high quality epitaxial  $\text{CoSi}_2$  films have been grown on Si (111) under UHV conditions by both standard deposition and MBE techniques. They and Ishiware and his coworkers<sup>5)</sup> have also demonstrated that epitaxial Si film overgrowth can be achieved on the heteroepitaxial  $\text{CoSi}_2$  film, which provides a new type of multistucture of  $\text{Si}/\text{CoSi}_2/\text{Si}$ .

$\text{CoSi}_2$  and  $\text{NiSi}_2$  have cubic structure ( $\text{CaF}_2$ ) similar to Si crystals.  $\text{NiSi}_2$  is an especially attractive candidate for high quality heteroepitaxy since it has much smaller lattice misfit ( $\sim 0.4\%$ ) to Si than  $\text{CoSi}_2$  ( $\sim 1.2\%$ ). However, only granular epitaxial films have been obtained to date. Recently, high quality  $\text{NiSi}_2$  films with very smooth surface morphology have been obtained

by precisely controlling metal and silicon beams<sup>6)</sup>. That is to say, stoichiometric deposition of Ni and Si allows  $\text{NiSi}_2$  heteroepitaxial growth on atomically clean surfaces at temperatures as low as  $550^\circ\text{C}$ . Figure 3 shows RHEED patterns and Nomarski microphotographs of grown films. The film is featureless, and extremely sharp RHEED patterns including diffraction spots and Kikuchi lines are observed. It should also be pointed out that the epitaxial temperature of  $\text{NiSi}_2$  in MBE growth is far below the minimum formation temperature ( $775^\circ\text{C}$ ) of conventional methods. It is well known that

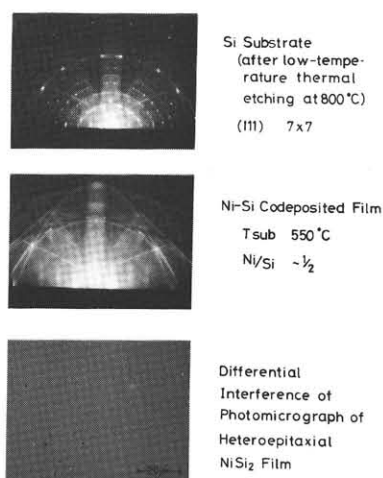


Fig. 3 RHEED patterns and surface morphology of MBE-grown  $\text{NiSi}_2$  films.

$\text{NiSi}_2$  is grown as a final phase at higher temperatures following the formation of  $\text{Ni}_2\text{Si}$  and  $\text{NiSi}$  films. However, in the case of MBE,  $\text{NiSi}_2$  is directly formed at lower temperatures without formation of the preceding phases. Cleanness throughout the whole process is crucial and may play an important role in interface reaction.

By formation of single crystalline silicide films on Si substrates, the electrical resistivity can be reduced much lower than those of polycrystalline silicides. For example, the resistivity of single crystal  $\text{CoSi}_2$  was measured to be  $10 \mu\Omega\text{cm}$ <sup>4)</sup>, the lowest ever achieved for any silicide thin films, and approaches that of pure cobalt ( $9.8 \mu\Omega\text{cm}$ ). This property may have a significant impact on silicon devices and technology.

Another interesting example of Si heteroepitaxy is the formation of such insulators as  $\text{CaF}_2$ . The growth of single crystal  $\text{CaF}_2$  on Si substrates by vacuum deposition of  $\text{CaF}_2$  grains has been shown<sup>7)</sup>. The heteroepitaxy of dielectric materials is of great interest because of its potential in realizing new novel devices such as three dimensional ICs.

#### 4. Device Application

A variety of Si MBE diode devices have been fabricated, such as a complex varactor diode in which the doping profile is designed to change as  $x^{-3/2}$ , a mixer diode for microwave use and so on. The mixer diode<sup>8)</sup> has a highly doped thin surface ( $150 \text{ \AA}$ ) layer which increases the field of the Schottky barrier, reducing the effective barrier height. Forward series resistance is also significantly reduced.

A buried channel MOSFET has been fabricated as an example of three terminal MBE devices<sup>9)</sup>. The channel mobility significantly exceeds the figure measured in a conventional buried-channel MOSFET fabricated with the aid of ion implantation. An NPN bipolar transistor with uncompensated base and emitter regions<sup>10)</sup> is another example of transistor structure. Because no thermal diffusion steps are involved, junction location and base width are precisely defined. Narrow base designs are expected to be developed and ultrahigh speed bipolar transistors will be fabricated by MBE.

Recently, poly-Si films have been demonstrated to be a promising material for thin film transistors and applicable not only to switching elements but also to driving circuits for liquid crystal displays. Si MBE can provide poly-Si films on conventional glass at moderately low temperatures. TFTs with the highest field effect mobility ( $\sim 40 \text{ cm}^2/\text{Vsec}$ ) among poly-Si TFTs have been fabricated using the MBE method and low temperature processes<sup>11)</sup>. Since new Si MBE machines are now being developed with emphasis being placed on such factors as sample size and throughput, large scale TFT matrix will be realized in the near future.

There are some proposals concerning Si-MBE application to new devices. When the scale of the LSI is greatly expanded and the size of individual

elements is greatly reduced, several device characteristics are known to be altered. To solve such problems as punch-through and  $V_{th}$  shift in short channel MOSFETs, an atomic-layer doped (ALD) impurity-profile has been proposed which can be achieved through Si-MBE<sup>12)</sup>. In this device, there are two heavily doped thin layers, with thicknesses of less than several hundred Å. These layers act as a punch-through stopper. As a result, ALD-MOSFETs have normal transistor characteristics even with the short ( $<1\ \mu\text{m}$ ) channel geometry.

Metal/silicon heterostructures have the potential for allowing formation of a variety of new devices with buried metal layers in semiconductor crystals. In the case of a permeable base transistor, where a grid-shape control electrode is buried in semiconductors like a triode tube, Schottky barriers are used to control electron current through the grid opening. The thickness and opening of the buried grid-shape base electrode are in the range of several hundreds, and some thousands of angstroms, respectively. It will be possible to develop such a transistor, through the combination of semiconductor/metal/semiconductor heterostructure formation and fine pattern process technology.

## 5. Conclusion

The feasibility of Si-MBE has been discussed in this review. The strengths are attractive enough to encourage researchers to extend their work in many fields, from basic studies on crystal growth mechanism to the development of new devices. Research will extend to crystal growth on such complex surfaces as those of LSIs. Figure 4 shows preliminary experimental results of selective MBE growth on patterned substrates.

As MBE is a typical dry process technique, it is quite feasible to combine MBE with plasma, radical or charged particle beams which are already being utilized in the latest process technology. Such a combination would lead to the extension of MBE use, as well as the achievement of a new dry LSI-process.

Finally, it should be pointed out that such Si-MBE strengths depend strongly upon improvement in ultrahigh vacuum technology. Researchers are continuing to perfect MBE processing, as well as

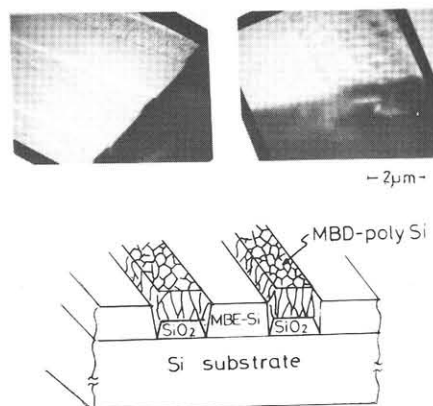


Fig. 4 Si-MBE growth on patterned substrates.

study MBE related surface and interface phenomena.

This review includes work performed under the management of the R and D Association for Future Electron Devices as a part of the R and D Project of Basic Technology for Future Industries sponsored by Agency of Industrial Science and Technology, MITI.

- 1) A. Ishizaka et al.; MBE-CST-2 (Tokyo, 1982) p.183
- 2) Y. Shiraki et al.; J. Crystal Growth 45, 287 ('78)
- 3) Y. Sugiura; J. Appl. Phys. 51, 2630 ('80)
- 4) R. T. Tung et al.; Thin Solid Films 93, 77 ('82)
- 5) S. Saitoh et al.; Appl. Phys. Lett. 37, 203 ('80)
- 6) A. Ishizaka et al.; to be reported at this conf.
- 7) T. Asano et al.; Thin Solid Films 93, 143 ('82)
- 8) W. C. Ballamy et al.; Appl. Phys. Lett. 39, 629 ('81)
- 9) Y. Katayama et al.; Appl. Phys. Lett. 34, 740 ('79)
- 10) R. G. Swartz et al.; IEEE EDL-2, 293 ('81)
- 11) M. Matsui et al.; J. J. Appl. Phys. 22, ('83) Sup. 22-1
- 12) K. Yamaguchi; J. J. Appl. Phys. 22 ('83) Sup. 22-1