PART I

Ion Assisted Deposition

IMPORTANCE OF SURFACE PREPARATION IN DIRECT ION BEAM DEPOSITION(IBD)

KIYOSHI MIYAKE
Hitachi Research Laboratory, Hitachi Ltd.
2046 Kuji-cho, Hitachi-shi
Ibaraki 319-12 Japan

ABSTRACT

Fundamental aspects of direct ion beam deposition (IBD) are discussed, stressing surface preparation and contamination problems. Residual gas contamination, ion beam induced metal contamination, and presence of surface native oxide before deposition are shown to be the major factors hindering low temperature epitaxial growth in IBD.

A low energy hydrogen ion bombardment is demonstrated as an effective surface preparation method to remove surface native oxide in the case of silicon deposition.

INTRODUCTION

Industrial applications of ion beams and plasmas for film formation have been expanded significantly in the last decade[1]. However, the actual surface chemical processes occurring in the ion/plasma-assisted film formation methods have not yet been clearly understood because film formations are carried out in thermally nonequilibriated complicated situations. Hence, mass- and energy-selected metal ion beams have been employed for film formation in order to investigate these complicated ion/plasma assisted film growing processes in a simpler manner. This method is known as "direct ion beam deposition (IBD)" and it has been studied intensively by many researchers[2-6].

To date, films of metals, as well as semiconductor materials, have been deposited by the IBD method by over 15 groups, working worldwide, using different types of IBD systems[3-29]. Epitaxial growth of silicon has been studied by a number of them[6,15-20]. In spite of the simplicity of the IBD method, however, it is rather difficult to conclude the general principles which govern the Si epitaxial growth, in part because handling of the ion beam differs significantly in each IBD system. Furthermore, the crystalline properties of the deposited films depend strongly on the surface preparation and the ion beam handling during deposition.

In this paper we try to make use of our Ge and Si epitaxial growth results obtained in two types of IBD systems in order to clarify surface preparation and contamination problems. A new surface cleaning method, utilizing low energy hydrogen ion beam bombardment, is shown to be effective in removing surface oxide layer on Si substrates.

Mat. Res. Soc. Symp. Proc. Vol. 157. ©1990 Materials Research Society

ENERGY RANGE USED IN IBD

The ion energy region used in IBD is, in principle, determined by the competitive phenomena between deposition and sputtering due to the incoming metal ions. That is, low energy metal ions efficiently deposit on a solid surface to form a film, whereas ions whose energy is higher than the threshold energy for sputtering (around 25 eV for Si) cause sputtering of both the substrate and deposited film. Therefore, the maximum critical energy for film formation in the IBD is primarily determined by the one which gives a self-sputtering yield of unity.

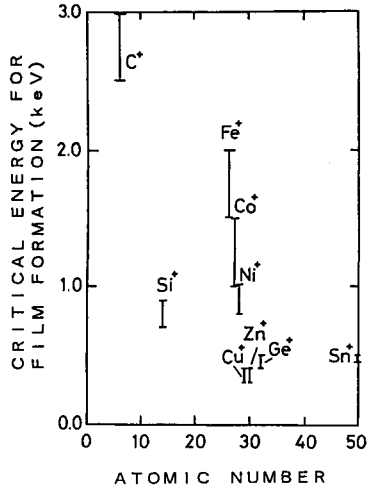

Fig. 1. Critical energies for film formation in IBD in the case of C, Si, Fe, Ni, Co, Ge, and Sn deposition.

The experimentally determined critical energies for IBD for a number of materials are shown in Fig. 1[2,8,16,29]. Large experimental error bars indicate the experimental difficulties in obtaining such low energy metal ion beams. Usually ion energies of 0.1-0.2 keV or less are employed for IBD studies. How to obtain a large amount of low energy metal ion beam is one of the most important and difficult points facing workers in carrying out IBD experiments. The most popular way is to extract a large current ion beam from an ion source at high energy, and to decelerate the mass-selected ion beam after mass separation to the desired deposition energy below the critical energy for IBD.

TWO TYPES OF HITACHI's IBD MACHINES

We constructed two types of IBD machines((I) and (II)) for Ge and Si epitaxial growth study. The schematics of the systems are shown in Figs. 2 and 3, respectively. The first one, (I), employed a two step ion beam deceleration method. Si or Ge ion beams generated in a duoplasmatron ion source were extracted at an energy of 16.5 keV and mass-separated by a magnet. The mass separated ion beam, with a kinetic energy of 16.5 keV, was first decelerated to 3 keV at the exit of the magnet and after traveling through the drift tube, it was finally decelerated to 0.1 keV on the substrate surface. Si^+ and Ge^+ ion currents of 4-5 uA were obtained in an ion energy region from 0.1 to 3.0 keV. The vacuum pressure during deposition was 1.3×10^{-3} Pa.

The second system (II), as shown in Fig. 3, was much improved by employing a modified Freeman-type ion source and a UHV pumping system. Ion beam deceleration was done only once for the mass-separated ion beam just in front of the substrate surface using an E x B type deceleration lens system. The lens system could effectively remove space charge neutralizing electrons contained in high current ion beams. An ion current of over 200 uA for the mass-selected $^{28}Si^{+}$ ion beam was obtained at an ion energy of 0.1 keV. The vacuum pressure during deposition was 6.5×10^{-6} Pa with a base pressure of 1.3×10^{-8} Pa.

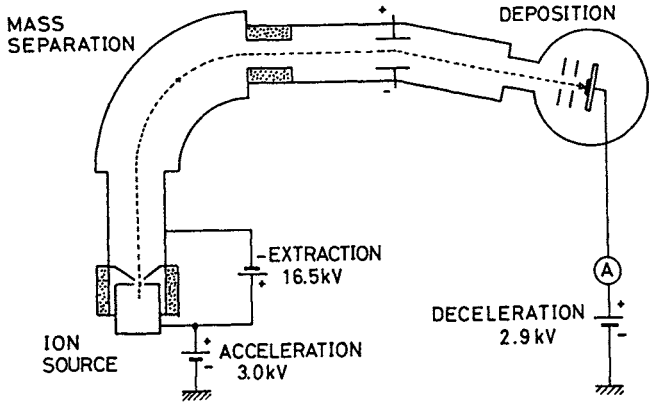

Fig. 2. Schematic of Hitachi's IBD machine(I)

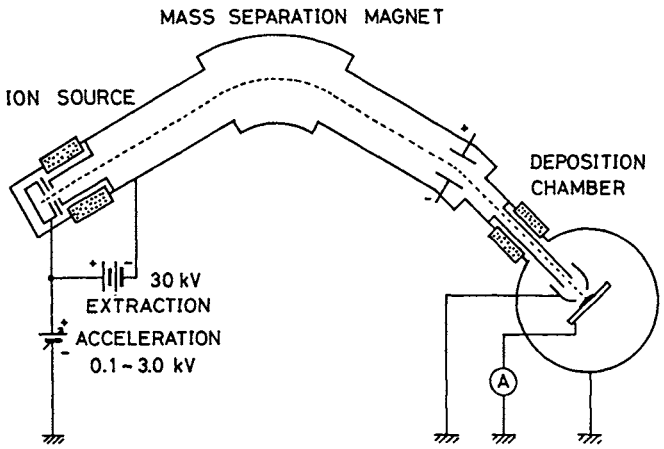

Fig. 3. Schematic of Hitachi's IBD machine(II).

RESIDUAL GAS CONTAMINATION AND EPITAXIAL GROWTH

In direct ion beam deposition, the surface under ion bombardment becomes chemically active. Therefore, in order to realize low temperature epitaxial growth of semiconductor materials it becomes necessary to minimize the sticking of residual gas molecules (in particular, oxygen adsorption due to water vapor is usually the severest), i.e. we need:

$$S_i G_i >> S_n G_n, \qquad (1)$$

where S_n and S_i are the sticking probability of the residual gas molecules and the incoming ions, respectively, and G_i and G_n are the incident fluxes of the residual gas molecules and the incoming ions, respectively.

G_i and G_n are calculated from the ion current density, J_i, and the residual gas pressure, p, as

$$G_i = 5.3 \times 10^{12} J_i(uA/cm^2) \quad (ions/cm^2.s), \qquad (2)$$

and

$$G_n = 6.5 \times 10^{20} p(Torr) \quad (molecules/cm^2.s). \qquad (3)$$

The operating regions of our two IBD systems are indicated in Fig. 4 along with those of recent IBD studies done at ORNL[4], Philips[5], and University of Salford[6].

In our first IBD system, (I), the ratio of the incoming ion flux to the residual gas flux was 10^{-2}[16]. In this case, epitaxial growth of germanium film on germanium substrate was possible at the substrate temperature of 300 °C. However, epitaxial growth of silicon was unsuccessful. IBD Si-films showed amorphous or polycrystalline structure and contained carbon contamination. This difference was thought to come from the lower sticking probability of oxygen and carbon on the germanium surface compared with the case on silicon.

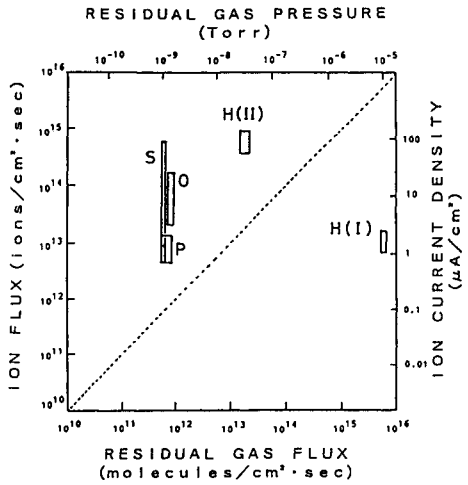

Fig. 4. The operating regions of IBD studies done at Hitachi(H(I), H(II)), ORNL(O), Philips(P), and University of Salford(S)[4,5,15, 16,17].

Epitaxial growth of silicon was made possible in the second IBD system, (II), in which the ratio of the incoming ion flux to the residual gas flux was 10^2[17]. A $^{28}Si^+$ ion beam was deposited on Si(100) substrate at a substrate temperature of 740 °C. No specific surface cleaning treatment was employed to remove surface native oxide. TEM observation of the Si-IBD film showed that it was a single crystalline material with a twin structure and it contained much dislocation damage. The reason why silicon epitaxial growth became possible in the second IBD system was attributed to the relative increase in the ion flux to the residual gas flux. That is, reduction of surface contamination due to residual gas adsorption during deposition was thought to be the main reason. Thus, when we discuss the crystalline properties of the deposited Si films, we have to consider other effects such as inclusion of metal contamination in the film or how the initial Si surface was cleaned before deposition.

METAL IMPURITY INCLUSION AND ION BEAM REFLECTION DURING DECELERATION

The epitaxially grown ^{28}Si film deposited in our second type IBD system (II) was analyzed by a SIMS method to investigate the metal impurity inclusion. For the deposition, the $^{28}Si^+$ ion beam was decelerated from 30 keV to 0.1 keV. The results shown in Fig. 5 revealed the inclusion of metals such as iron and chromium, which are the main constituents of stainless steel. As shown in Fig. 5(b), the SIMS mass spectrum for the Si(100) substrate reference showed Si-related typical mass peaks at m/e = 14($^{28}Si^{++}$), 28($^{28}Si^+$), 29($^{29}Si^+$ + $^{28}Si^1H^+$), 30($^{29}Si^1H^+$), 44($^{28}Si^{16}O^+$), 56($^{28}Si_2^+$). The relative ratio of ^{28}Si, ^{29}Si, ^{30}Si agreed well with the natural abundance of silicon isotopes (92.23 : 4.07 : 3.10). On the other hand, the SIMS spectrum for the $^{28}Si^+$ ion beam deposited films shown in Fig. 5(a) indicated peaks at m/e = 14, 28, 29, 44, 52, 56. This spectrum meant that the film was isotopically enriched with ^{28}Si. Neither ^{29}Si nor ^{30}Si were present in the film. The mass peak at m/e = 29 corresponded to $^{28}Si^1H$. The mass peaks which appeared at m/e = 52 and 56 were assigned to ^{52}Cr and ^{56}Fe after subtracting the predicted $^{28}Si_2^+$ contribution (Fig. 5b). Quantitative estimation of the impurities was rather difficult from the SIMS results only.

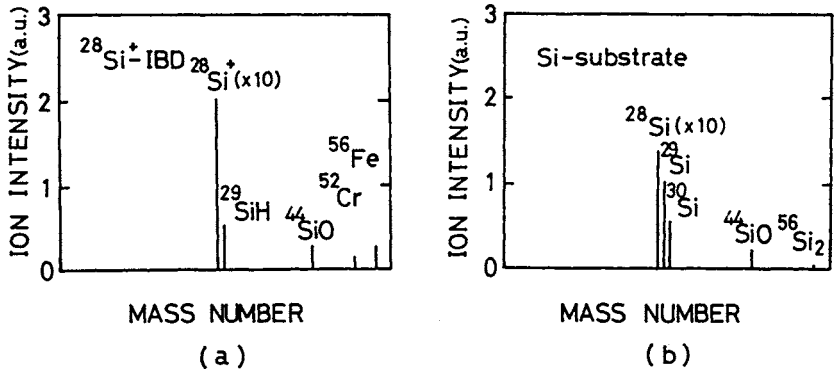

Fig. 5. SIMS mass spectra for the (a)Si-IBD film and (b) Si substrate as a reference.

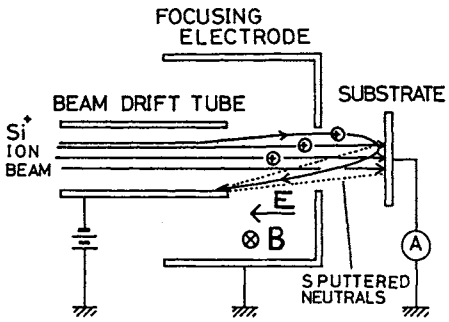

Fig. 6. Ion beam behavior using an E x B type deceleration lens system.

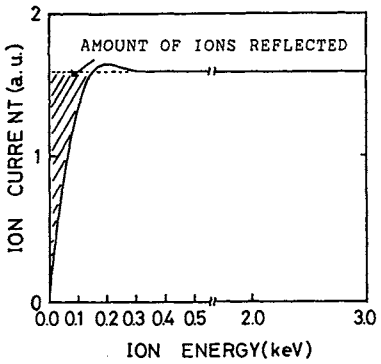

Fig. 7. A typical decelerated ion current vs. ion energy characteristics.

In order to investigate the reason for such metal impurity inclusion, the ion beam behavior during deceleration was directly observed and it was found that part of the incoming ions were reflected in front of the substrate. They were reaccelerated toward the opposite direction as shown in Fig. 6 causing them to hit the drift tube electrode, which was made of stainless steel. Since the impinging energy was as large as 30 keV, production of sputtered neutrals like iron and chromium would be expected.

This was also in good agreement with the decelerated ion current vs. ion energy characteristics as shown in Fig. 7. In the direct observation of the ion beam behavior during deceleration, we confirmed that the space charge repulsion of the ion beam was not important. Instead, because of the energy spread of the incoming ion beam and the non-perpendicular incidence of the incoming ion beam, part of the incoming ion beam was reflected in front of the substrate. This fact corresponded to the decrease of the decelerated ion current below 0.1 keV in Fig. 7 and also supported the generation of sputtered impurity particles. The hatched region in the figure corresponds to the number of ions reflected.

Since in IBD, film formation is done only by ionized particles, the presence of such sputtered neutral impurity particles causes the degradation of the crystalline features of the deposited films. One solution might be to make the electrodes of the same material as the depositing materials or to coat the electrodes with the same material as deposited.

Si SURFACE CLEANING BY HYDROGEN ION BOMBARDMENT

In the above epitaxial growth of Si, no special wafer treatment was employed to remove surface native oxide before deposition. This absence of surface precleaning was also thought to contribute to residual damage in the film. Therefore, suitable surface cleaning has become one of the fatal factors to the success of ion beam deposition.

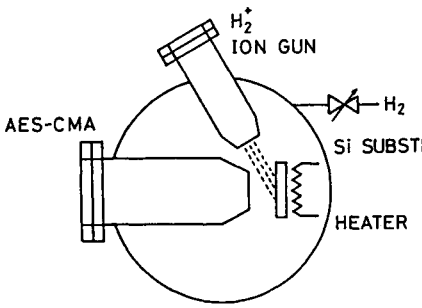

Fig. 8. Schematic of ion beam surface cleaning system.

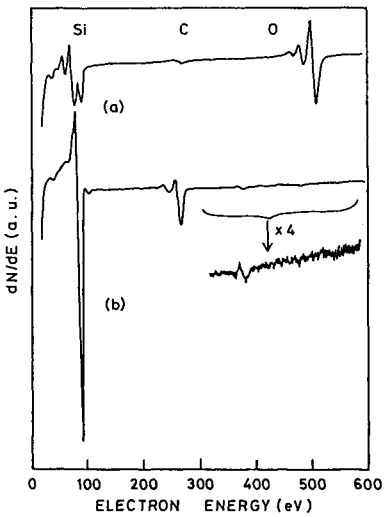

Fig. 9. Changes in AES spectra for the 10 nm SiO_2/Si substrate (a) before and (b) after hydrogen ion bombardment for 10 min at 450°C. Ion energy and ion current were 1.0 keV and 20 uA, respectively.

We examined a Si surface cleaning method for removal of surface oxide by hydrogen ion bombardment. The experiments were carried out in the deposition chamber as shown in Fig. 8. The base pressure was 1.3×10^{-8} Pa. The samples were single crystalline Si(100) substrates covered with a 10nm thick thermal oxide layer, which simulated surface native oxide. A hydrogen ion beam was bombarded on the samples using an electron beam bombardment type ion gun in a H_2 gas pressure of 6.5×10^{-3} Pa. The ion beam diameter on the sample was about 6 mm and the beam energy was 0.5 or 1.0 keV. Substrates were heated from RT to 450 - 500°C. In-situ AES analysis was employed to monitor surface composition changes caused by the ion bombardments.

As shown in Fig. 9(a), the AES spectrum for the initial Si(100) substrate covered with 10nm thick thermal SiO_2 had a typical spectrum for an oxidized Si surface[31]: $Si_{L2,3VV}$ peaks at 78 eV (Si-O)and 92 eV (Si-

Si), and an O_{KL2L2} peak at 507 eV. Neither hydrogen ion bombardment at room temperature for 10 min with an ion energy of 0.5 keV nor post-annealing in a vacuum (436°C for 30 min) /hydrogen atmosphere (443°C for 10 min) gave an appreciable change in the AES spectrum.

In the case of hydrogen ion bombardment at elevated temperature (450-500°C), a drastic change was observed in the AES spectrum as shown in Fig. 9(b). Hydrogen ion bombardment was performed for 10 min at 450°C. Three different features appeared in the spectrum: the O-peak at 507 eV disappeared; the Si-peak shapes changed dramatically; and the C-peak at 270 eV appeared. The Si peak at 92 eV , which is due to Si-Si bindings, became much larger than the Si-peak at 78 eV, which is due to Si-O bonding. The appearance of the carbon peak at 270 eV seemed due to hydrocarbon contamination caused by outgas from the ion source. Irradiation with 1 keV hydrogen ions for 20 min at 495°C essentially removed the SiO_2 layer.

Neither physical nor chemical sputtering yields of SiO_2 by H_2^+ ion bombardments has been reported in the literature. Physical sputtering yields of silicon by H^+ ions have been reported to be on the order of 10^{-3} [32]. Assuming a similar yield for SiO_2, the thickness removed during the above irradiations should be on the order of 10^{-2} nm. So it would hardly be possible to attribute SiO_2 etching only to a physical sputtering effect. Moreover, the elevation of the substrate temperature during the ion bombardment accelerated the etching of SiO_2. Therefore, some chemical sputtering effect must be responsible for the SiO_2 etching[33].

The hydrogen ion bombardment method shown here has a potential use as an Si surface cleaning method, since the damage caused by hydrogen ion bombardment is probably small. Application of this surface cleaning method to Si ion beam deposition is the next step our work will take.

Conclusions

Fundamental aspects of direct ion beam deposition were discussed with a stress on impurity inclusion and surface preparation problems. It was shown that residual gas adsorption and sputter deposition of metal impurities during film growth were fatal factors hindering low temperature epitaxial growth of Si and Ge. In addition, a new Si surface cleaning method of using low-energy hydrogen ion bombardment at elevated temperature (450-500 °C) was proposed as effective in removing the SiO_2 layer before deposition.

Acknowledgments

The author acknowledges fruitful collaborations with Dr. K. Yagi, Prof. T. Tokuyama, and Mr. S. Tamura in the course of the IBD work. He also thanks Dr. A. Shintani for valuable discussions and useful comments on Si surface cleaning, and he acknowledges Mr. K. Natsui for his critical reading of the manuscript.

REFERENCES

1. For example, Physics of Thin Films, Vol.13 (Ed. by M.H. Francombe and J.L. Vossen, Academic Press, Inc., New York, 1987)