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"In-Situ" Electron Microscope Investigation of the Nucleation
and Growth of Sputtered Thin Films

by

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Summary

The study of silver and gold on single crystal substrates of silicon has uncovered an important feature of substrate-overgrowth interaction leading to alloy formation. This gives rise in both cases to films which must have much higher resistivity values than would be expected for non-interacting films of comparable thickness although they do form epitaxial films. Ion beam damage and annealing studies of the substrate clearly indicate the importance of careful annealing of silicon substrates in order to attain epitaxial recrystallization of the damaged silicon layer.

Silicon Substrates.

Silicon substrates suitable for in-situ deposition have been produced by the process of jet chemical polishing and ion beam bombardment. The detailed preparation procedure and the apparatus for polishing and ion bombardment were presented in the previous progress report (1973). Only the alteration of the crystal structure of silicon outer layer and the change of surface morphology caused by ion bombardment are discussed here.

The most important effect on the crystal structure by the impact of high energy ions, as far as the deposition of thin films is concerned, is the formation of an amorphous silicon layer. This ion-damaged layer will vary the growth and the final structure of thin films deposited on it. The formation of this amorphous layer is clearly indicated by the change in the electron diffraction pattern of the substrate. Diffuse rings appear after ion bombardment. The superposition of these diffuse rings over the sharp spots of single crystal silicon is shown in Figure 1(a). It means that the periodicity of the atomic arrangement of the outer layer disappears after ion bombardment, while the silicon underneath still remains crystalline, i.e. undamaged. Epitaxial recrystallization of the ion damaged layer occurs rapidly by annealing. Figure 1(b) shows the disappearance of the diffuse rings after annealing the ion bombarded silicon in the electron microscope hot stage at 600°C. On some extremely thin areas of the silicon chips, where the ion range is greater than the foil thickness, the electron diffraction pattern is composed only of diffuse rings after ion bombardment. Annealing may cause the formation of polycrystalline rings, but epitaxial recrystallization never occurs in these areas. Transformation of amorphous to single crystalline silicon of the substrates during annealing is believed to start from the interior regions where the damage by ion beam was less severe. This is illustrated in Figure 2. Thus epitaxial recrystallization

is not nucleated in the very thin areas, especially at the thin edge. Figure 3 is a micrograph of silver islands on an annealed silicon substrate. No extinction contour is observed at the thin edge. The density, size, and structure of the silver islands are also varied.

The change in the surface morphology of silicon brought about by ion bombardment is basically the formation of "hillocks." Figure 4(a) is a typical micrograph of the silicon substrates observed after ion bombardment. The hillocks have a quasi-hemispherical exterior and a smooth surface. The exterior shape of hillock depends, more or less, on the rotation of the substrate holder during bombardment. Feather-like hillocks occur on substrates which were not rotated during bombardment. These are shown in Figure 4(b). Experiments have been performed using the Commonwealth Ion Micro Milling Instrument to determine the causes of hillock formation. It has been found that their formation does not relate to the ion beam voltage and current in the range of this instrument, and depends neither on the purity of silicon nor on the existence of foreign impurities¹. However, ion beam incident normal to the silicon surface yield a flatter (no hillock formation) but rougher (severely damaged) surface. It is plausible to conclude that the hillocks are caused by the "oblique" incidence of the ion beam. In spite of the existence of hillocks, smooth flat areas with sizes of several microns and free from any surface irregularity are still abundant on the substrate, which are suitable for the observation of the nucleation and growth of thin films deposited upon them.

Silver on Silicon

The initial results of the in-situ deposition of silver on the (111) plane of single crystal silicon substrates were presented in the previous progress report (1973). The general features of the process of nucleation and growth were reported to be qualitatively the same as the deposition of

silver on mica and graphite. Continued investigations have been performed in this area. Although the arrangement for these in-situ experiments is identical to that used previously, new insight about the growth of silver films, especially during the islands coalescence stage, have been obtained, which have led to the discovery of a unique mode of thin film growth. This unique growth process can be divided into two stages. Each stage corresponds to the growth of one layer of islands. The growth of these two layers is to be discussed here.

Experiments were performed at substrate temperatures maintained from 440°C to 600°C and deposition rates from 20 to 50 Å/min. The size of the first detectable islands observed in these experiments was roughly 25 Å. Both the size and the number density of the islands increase with the deposition time. The saturation island density is of the order of 10^{11} to 10^{12} cm⁻² and is dependent upon the substrate temperature and deposition rate. These islands grow and touch their neighbors at a size of 50 Å - 100 Å. These silver islands (first layer islands) do not coalesce in a liquid like manner, nor does a pair of rounded islands transform suddenly into a single rounded island as they touch. These islands rather stay at their original positions when they touch with a boundary existent at the join. This growth process is shown in Figure 5. Neither rotation nor translation of islands has been observed.

After the formation of the clusters of contacting islands, liquid-like coalescence has been observed to occur and does become more pronounced as the film grows thicker. This is attributed to the growth of a second layer of silver upon the clusters of islands formed previously. Figure 6(a) and 6(b) show the occurrence of liquid-like coalescence on the areas indicated by an arrow. Boundaries of the initial islands which are under the second layer silver islands can still be seen at a very late stage in the deposition

process as shown in Figure 6(c).

An illustration to make this two layer growth process more understandable is given in Figure 7 where the particular growth of silver on silicon is compared with the case of growth normally observed². The growth of the first layer islands differs from normal case in that no motion or liquid-like coalescence occurs. This indicates a very strong bonding between the overgrowth and the substrate which may be due to the formation of an alloy-like structure at the interface of silver and silicon. The second layer silver grows on the first layer islands as a new surface has been created. Since the silicon can migrate through the silver film at elevated temperature³, it is possible to form a thin layer of silicon on the surface of the first layer islands. The prohibition of liquid-like coalescence of the first layer islands and the growth of the second layer silver upon the clusters of the first layer islands may be attributed to the formation of this thin silicon layer.

Auger analysis has been carried out with the help of Professor Wehner's group to determine the in-depth profile⁴ of silver and silicon concentration in the samples of both before and after the formation of the second layer. No unequivocal conclusion was obtained from this analysis regarding the formation of this thin silicon layer. It is possible that this silicon layer may be only several atomic layers thick, which is less than depth of analysis of Auger electron spectroscopy.

The hydro-carbon molecules in the high vacuum system may form a contamination layer on the silver islands, which may also have caused this two layer island growth to occur; nevertheless, the possibility is low, since this special growth phenomenon has not been found in the systems of silver on substrates such as amorphous carbon, mica, or graphite.

Experiments were performed at substrate temperatures of 350°C and 300°C

with a deposition rate of $20 \text{ \AA}/\text{min}$. At these temperatures, after a short period of sputter deposition, the islands have a density higher and an average size smaller than that deposited at higher substrate temperatures, so the islands can contact and coalesce with their neighboring islands at a much smaller size and to form an irregular periphery before the second layer islands begin growth upon them. A growth sequence at 350°C is given in Figure 8.

In all the experiments reported above, both the first and the second layers grow in an epitaxial orientation parallel to the single crystal silicon substrate. The epitaxial orientation is described by $(111) \text{ Ag} // (111) \text{ Si}$; $[\bar{1}\bar{1}0] \text{ Ag} // [\bar{1}\bar{1}0] \text{ Si}$. Epitaxial growth has been observed at substrate temperature as low as 260°C . No change in lattice constant of the silver films has been found before or after the formation of the second layer.

Depositions at 23°C , however, give a polycrystalline structure. The ring pattern of Figure 9(a) indicates that small silver grains with nearly random orientation grow on the (111) plane of single crystal silicon substrate. The micrograph of Figure 9(b) shows that the film is continuous (of the channel stage) and flat, which is unlike the epitaxial silver films deposited at higher temperature.

It has been mentioned in the previous section that ion beam thinning will cause thin layer of amorphous silicon to be formed on the single crystal silicon substrates. How this amorphous silicon layer affects the final structure of silver films is made clear by a comparison of Figure 10 and Figure 11. Figure 10 is a micrograph of a film deposited on a well-annealed single crystal silicon substrate; while Figure 11 is of a film on a substrate which was not annealed. Figure 11(a) shows that the silver film, instead of forming an epitaxial film as in Figure 10, results in a polycrystalline

structure with a preferred orientation of the Ag (111) plane parallel to the (111) plane of undamaged single crystal silicon which is under the amorphous layer. The existence of the faulted orientation is indicated by the variation of contrast inside some islands of Figure 11(b).

Gold on Silicon.

Gold has been sputter deposited on silicon substrates at temperatures ranging from 23°C to 500°C. The structure and growth of gold films have been found to vary greatly with the substrate temperature. In different temperature ranges, the films are found to be either amorphous, or polycrystalline, or even resident in the liquid state. At substrate temperatures lower than 300°C, the growth of gold films were not observed directly, since the hydrocarbon molecules in the vacuum system are decomposed by the electron beam of the microscope, which contaminate the substrates at these temperatures and affect the growth of thin films⁵. In all the experiments to be discussed here, the deposition rate is 20 Å/min.

At substrate temperatures 23°C - 130°C an amorphous film is first formed after 400 seconds of sputter deposition. This film can hardly be seen in the electron microscope, only the appearance of the diffuse ring in the electron diffraction pattern, as in Figure 12(a), shows its formation. At later stages in the deposition, roughly 600 Å means thickness, a polycrystalline island structure becomes dominant as shown in Figure 12(b) and 12(c). These gold islands are believed to grow on the amorphous film formed earlier.

At temperatures 160°C - 200°C the growth of sputtered gold films on silicon substrates results in the formation of some peculiar micro-sized islands after 400 seconds of deposition as shown in Figure 13. These islands are polycrystalline as shown by the selected area electron diffraction pattern.

The adjacent areas are amorphous as indicated by the diffuse ring diffraction pattern. The internal features of these micro-sized islands are shown clearly in Figure 13(b).

At substrate temperatures 300°C - 500°C the growth and the structure of gold films can be described as perfectly "liquid-like." The growth process at this temperature range can be represented by two sequences of micrographs shown in Figure 14 and Figure 15. The nuclei of these films form islands nearly hemispherical, and the islands coalesce in a manner like the coalescence of two drops of water. The structure of these islands is indicated by the electron diffraction patterns (b) and (c) of Figure 16. The change from the diffuse ring pattern in (c) to the polycrystalline pattern in (d) occurs at 260°C by lowering the substrate temperature after deposition. The island structure of Figure 17 also shows the crystallization of gold films after being cooled down to room temperature. Since the eutectic temperature of Au-Si system is only 370°C, the islands shown in Figure 14 and Figure 15 are believed to be the liquid alloy of gold and silicon. The cooling rate of the substrate in the electron microscope hot stage is less than 5°C/sec, the silicon in the liquid eutectic alloy can grow epitaxially during cooling on the underlying single crystal silicon substrate⁷.

At 240°C substrate temperature, both liquid islands and solid islands coexist on the silicon substrates after 400 seconds of sputter deposition.

Ultra High Vacuum In Situ Deposition System

The work on the construction of the ultra high vacuum in situ deposition system was completed recently. The appearance of this system is shown in Figure 18. This assembly, although appearing rather complicated, can be described clearly by dividing it into three major parts. These three parts are (1) ultra high vacuum chamber (Figure 19), (2) vacuum pump assembly

(Figure 24), and (3) electron microscope column.

The ultra high vacuum chamber is isolated from the condenser lens above and the objective lens below by two apertures. These apertures maintain a pressure difference between the chamber area and the microscope column, while allowing the electron beam to pass through the chamber. This differential pumping principle is the basis of the design of this ultra high vacuum chamber used for in situ deposition. The thin film deposition arrangement in this chamber includes an ion source, a target, and a substrate holder. Figure 20(a) shows the duoplasmatron ion source for ultra high vacuum sputter deposition. The position of this ion source, after being attached to the chamber, is shown in Figure 20(b). The target for thin film deposition is mounted on a $2\frac{3}{4}$ " ConFlat flange as shown in Figure 21. The heater cone, which is used for holding and heating the substrate during in situ deposition is shown in Figure 22(a). The substrate resides near the tip on the inside of the cone. The substrate temperature is measured by a tungsten-rhenium thermocouple which is spot welded to a tantalum ring pressed upon the substrate. The stage for the heater cone is shown in Figure 22(b), which can be transversed in four directions. A quadrupole mass spectrometer is also attached to the ultra high vacuum chamber, as shown in Figure 23(a). It is basically used to determine the residual gas pressure in the chamber area, however, it can also be used to monitor the atomic species sputtered from the target by ion beam. A typical mass spectrum given by this spectrometer is shown in Figure 23(b).

The vacuum pump assembly include a Granville-Phillips series 220 Electro Ion pump and a NRC VHS-6 diffusion pump. The Electro Ion pump has a high pumping speed for active gases, while the diffusion pump has a very high speed for inert gases, which is used for the purpose of pumping the argon gas introduced into the system during ion beam sputtering. The

diffusion pump is connected to the ultra high vacuum chamber via a 6-inch high conductance liquid nitrogen trap, a 8-inch O.D. elbow, and a T coupling, these are shown in Figure 24. Two pressure activated gate valves isolate both the diffusion pump system and the Electro Ion pump from the main chamber. An initial vacuum test shows that a chamber pressure of lower than 9×10^{-9} torr can be obtained by this vacuum pump assembly without baking the system.

The final work on this ultra high vacuum system is the alignment of microscope column after assembly. The alignment procedure of this system is much more complicated than on the conventional electron microscope. The difficulty is mainly due to the adjustment of the position of lower chamber aperture which has a diameter of only 250μ . The position of this aperture can only be adjusted from the bottom of the chamber, which means the chamber must be disconnected from the vacuum pump assembly and be raised up from the lower part of the microscope column. A micrograph of a carbon grating replica (54,800 lines/in) taken after the alignment of this system, is shown in Figure 25.

Discussion of Results

In both studies of nucleation of growth of gold and silver on substrates of silicon show the very clear influence of substrate-overgrowth interaction. In the case of silver-silicon it appears that at temperatures greater than 300°C an alloy is formed which greatly reduces the surface diffusion of the atoms over the nucleus and, further, impedes gross motion of the nuclei over the substrate thus retarding coalescence. The overgrowth is however epitaxial in a lattice parallel configuration.

The second layer growth is also epitaxial with "normal coalescence behavior". This unique two step growth process is highly interesting from considerations of formation of thin film conductors on silicon chips in commercial applications. The very thinnest films will have very high resistance values due to the large number of grain boundaries in the coalescence impeded film. As the second layer is formed the resistance will drop as normal coalescence processes form a larger grained structure. Room temperature deposits will be high in resistance at all thicknesses since they are polycrystalline and show no evidence of alloy formation.

Resistance of thin gold films will also be very high for low temperature amorphous and polycrystalline deposits.

The importance of substrate preparation is clearly illustrated in the ion beam damage studies. Annealing at temperatures greater than 600°C is required to attain epitaxial recrystallization which renders the substrate single crystalline again. The hillock formation during thinning while causing little trouble for nucleation studies should certainly be considered in silicon device cleaning and preparation. Nonuniformity in the substrate can give rise to device failure.

The performance of the ultrahigh vacuum stage in its first tests is

most gratifying. The studies of highly oxidation sensitive systems such as niobium and CdS can now proceed in a controlled way with a clean and well monitored (mass spectrometer) environment.

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Figure Captions

- Figure 1.(a) Electron diffraction pattern of ion bombarded silicon before annealing in the electron microscope hot stage.
- (b) Electron diffraction pattern of ion bombarded silicon after annealing in the electron microscope hot stage at 600°C.
- Figure 2. Illustration of amorphous layer formation and epitaxial recrystallization caused by ion bombardment and annealing respectively. Crosshatched areas are single crystalline.
- Figure 3. Silver islands on both the single-crystalline and the amorphous regions of silicon substrate after one minute of sputter-deposition. The substrate was at 520°C and the deposition rate was 20 Å/min.
- Figure 4.(a) Formation of hillocks on silicon substrate by ion beam bombardment.
- (b) Same as (a), except that the substrate was not rotated during ion beam bombardment.
- Figure 5. Growth sequence of the first layer of silver islands on silicon substrate at 600°C. The deposition rate was 50 Å/min. (a) 125 sec.; (b) 163 sec.; (c) 203 sec.
- Figure 6. Liquid-like coalescence of the second layer of silver islands. The substrate was at 440°C and the deposition rate was 20 Å/min. (a) 1164 sec.; (b) 1169 sec.; (c) 1850 sec.
- Figure 7.(a) Thin film growth process normally observed.
- (b) Two layer island growth of silver on silicon.
- Figure 8. Growth sequence of silver on silicon at substrate temperature 350°C and deposition rate 20 Å/min. (a) 49 sec.; (b) 90 sec.; (c) 187 sec.; (d) 312 sec.; (e) 510 sec.; (f) 762 sec.
- Figure 9.(a) Electron diffraction pattern and
- (b) Micrograph of silver on silicon after 400 sec. of sputter deposition. Substrate temperature was 23°C and deposition rate was 20 Å/min.
- Figure 10(a) Electron diffraction pattern and
- (b) Micrograph of 130 Å silver film deposited on silicon substrate at 425°C. The substrate was annealed to 600°C before deposition.
- Figure 11(a) Electron diffraction pattern and
- (b) Micrograph of 130 Å silver film deposited on silicon substrate at 425°C. The substrate was not annealed before deposition.

Figure 12(a) Electron diffraction pattern of 130 Å gold film deposited on silicon substrate at 23°C.

(b) Electron diffraction pattern at 600 Å gold film deposited on silicon substrate at 23°C.

(c) Micrograph of the gold film in (b).

Figure 13(a) Electron micrograph and selected area electron diffraction patterns of 130 Å gold films deposited on silicon substrate at 160°C. The micro-sized island shows polycrystalline structure while other areas only give a diffuse ring of amorphous structure.

(b) Electron micrograph printed at a reduced exposure shows the inner features of the islands in (a).

Figure 14. Gold sputter-deposited on silicon substrate at 500°C. The deposition rate was 60 Å/min. (a) 118 sec.; (b) 261 sec.; (c) 391 sec.; (d) 875 sec.

Figure 15. Gold sputter-deposited on silicon substrate at 300°C. The deposition rate was 20 Å/min. (a) 281 sec.; (b) 309 sec.; (c) 358 sec.

Figure 16. A sequence of electron diffraction pattern of gold film sputter-deposited on silicon substrate at 500°C. The deposition rate was 20 Å/min. (a) 0 sec.; (b) 210 sec.; (c) 875 sec.

Figure 16(d) Polycrystalline ring pattern of gold film.

Figure 17. 200 Å gold film deposited on silicon substrate at 300°C. This micrograph was taken after the gold film had been cooled down to room temperature.

Figure 18. Ultra high vacuum in situ deposition system.

Figure 19. Ultra high vacuum chamber.

Figure 20(a) Duoplasmatron ion source for UHV sputter deposition.

(b) Duoplasmatron ion source after being attached to UHV chamber.

Figure 21. Target for UHV in situ sputter deposition.

Figure 22(a) Heater cone for holding and heating of substrate during in situ deposition.

(b) Stage for holding and transversing the heater cone.

Figure 23(a). Quadrupole mass spectrometer.

(b) A typical spectrum obtained by this mass spectrometer.

Figure 24. Vacuum pump assembly.

(a) Liquid nitrogen trapped diffusion pump, elbow, and gate valve.

(b) T coupling, gate valve, and Electro Ion pump.

Figure 25. A micrograph of carbon grating replica (54,800 lines/in) taken after the alignment of electron microscope column.

(a)

(b)

Figure 1

Before Ion Bombardment

After Ion Bombardment

After Annealing

Figure 2

0.5 μ

Figure 3

(a)

(b)

Figure 4

(a)

(b)

(c)

0.1 μ

Figure 5

(a)

(b)

(c)

0.1 μ

Figure 6

(a)

(b)

Figure 7

(a)

(b)

(c)

(d)

(e)

(f)

0.1μ

Figure 8

(a)

(b)

0.1μ

Figure 9

(a)

(b)

0.1μ

Figure 10

(a)

(b)

0.1μ

Figure 11

(a)

(b)

0.1μ
(c)

Figure 12

(a)

(b)

0.5 μ

Figure 13

(a)

(b)

(c)

(d)

0.5 μ

Figure 14

(a)

(b)

(c)

0.1 μ

Figure 15

(a)

(b)

(c)

(d)

Figure 16

0.5 μ

Figure 17

Figure 18

Figure 19

(a)

(a)

Figure 20

Figure 21

(a)

(b)

Figure 22

(a)

(b)

Figure 23

(a)

(b)

Figure 24

Figure 25