ANNUAL TECHNICAL PROGRESS REPORT VII

"IN-SITU" ELECTRON MICROSCOPE INVESTIGATION OF THE NUCLEATION
AND GROWTH OF SPUTTERED THIN FILMS

by

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Introduction

The ultrahigh vacuum sputter deposition system referred to in 1974 progress report has been installed for studies of the nucleation and growth of ion beam sputtered thin films in a well controlled environment. The data obtained under these conditions have shown significant divergence from the data obtained in previous moderate vacuum of 10^{-6} torr due to active gas interaction.

Gold has been sputter deposited on substrates of single crystal silicon in vacuum of 1×10^{-8} torr. The results obtained show that the low eutectic temperature of Au-Si system and strong substrate/overgrowth interactions involving alloying and interdiffusion do not allow epitaxy. These data are correlated in terms of the masking effect of residual gases with the data previously obtained under less well controlled conditions. The electron irradiated area was compared with other substrate areas during the deposition process and after deposition was terminated in order for determining the influence of the imaging electron beam on the nucleation and growth of thin films.

A review of epitaxial growth and structure of CdS films has been done during past year. Ultrahigh vacuum in situ electron microscopic investigation of the nucleation and growth characteristics of ion beam sputtered cadmium sulfide on substrates of single crystal silicon will be completed in the next contract period. CdS films on semi-conductor slices are of potential value for acoustoelectric and surface wave devices. Commercial use in solid state electronic devices is not possible, however, because they are not available as crystals of the required purity and perfection. This and an intrinsic interest in the nucleation

kinetics provide practical reasons for a systematic investigation of the growth and structure of CdS films.

Ultrahigh Vacuum Sputter Deposition System

The ultrahigh vacuum deposition system, which is shown in Figure 1, can be divided into three major parts: ultrahigh vacuum chamber, vacuum pump assembly, and electron microscope column. Each of these was described in detail in the previous progress report VI. Short comments are given for the schematics of the ultrahigh vacuum deposition system.

A cross section of the hot stage assembly and apertures of the ultrahigh vacuum specimen chamber is shown in Figure 2. A liquid nitrogen cooled low conductance copper tube (upper aperture) and a 250 μm Pt aperture (lower aperture) isolate the metal sealed ultrahigh vacuum chamber from the 10^{-5} torr microscope vacuum systems, and maintain a pressure differential between the chamber area and the microscope column.

The specimen heater cone and thermocouple of the ultrahigh vacuum hot stage assembly are shown in Figure 3. The substrate temperature is measured by a Pt-Rh/Pt thermocouple which is spot-welded on a tantalum ring pressed upon the edge of the substrate.

A schematic of the ultrahigh vacuum in situ deposition system is shown in Figure 4. The duoplasmatron ion source is welded to a six-inch ConFlat flange. The partial pressures of the residual gases in the chamber are measured by the quadrupole mass spectrometer. Figure 5(a) shows that before adding liquid nitrogen into the reservoir (chamber cold ring), the partial

pressures of hydrocarbons and water vapors are quite high. After introducing liquid nitrogen into the reservoir, the partial pressures of hydrocarbons and water vapors are largely reduced as shown in Figure 5(b). During sputter-deposition, the chamber pressure is in the range of $5-7 \times 10^{-6}$ torr, which is mainly due to the partial pressure of argon, as shown in Figure 5(c). The pressure due to other residual gases is in the 10^{-8} torr range.

Gold on Silicon

Gold has been sputter deposited on substrates of single crystal silicon at temperatures ranging from 23°C to 500°C in vacuum of 1×10^{-8} torr. The deposition rate was 15 Å/min in all the following experiments. The structure and growth of sputtered thin gold films has been found to vary grossly with the substrate temperature in a manner qualitatively dissimilar to that obtained in vacuum of 10^{-6} torr.

The substrate temperatures can be divided into two regions at a temperature of roughly 200°C, which is believed to be the eutectic temperature of gold and silicon in thin films: the low and high temperature regions.

At low substrate temperatures, below 200°C, an amorphous film is first formed. The limited capabilities of our observational method do not allow to detect very thin continuous amorphous layers. This can only be seen from the appearance of the diffuse ring in the electron diffraction pattern as shown in Figure 6(a) after 400 seconds of sputter deposition. At later stages in the deposition, roughly 400 Å mean thickness, polycrystalline gold

islands grow on the amorphous layer formed earlier. Figure 6(b) shows the diffraction pattern of the polycrystalline gold islands. This growth process is shown in a series of micrographs in Figure 7. The average size of the polycrystalline gold islands has been found to vary with the substrate temperature. At temperatures in the range 23-120°C, the resultant deposit morphology is an island structure of fine grain. At temperatures 120-200°C, the growth of sputtered gold islands on silicon substrates results in the formation of two dimensional micro-sized polycrystalline gold islands followed by a network (Figure 7(c)). Transformation of the electron diffraction pattern from the polycrystalline gold rings to the diffuse ring of the liquid alloy of gold--silicon occurs at around 200°C by heating the substrate over the eutectic temperature after deposition (Figure 6(c)). Reverse transformation from the diffuse ring to the polycrystalline gold rings occurs upon cooling the substrate down to the room temperature (Figure 6(d)).

At high substrate temperatures, above 200°C, liquid and polycrystalline islands are formed nearly simultaneously on the substrate. These islands grow and coalesce in a manner identical to that of liquid, and have a nearly hemispherical morphology as shown in a long series of micrographs in Figure 8. It has been found by the dark field electron microscopy that the polycrystalline regions are formed inside the liquid islands. A series of the electron diffraction patterns in Figure 9 shows that the polycrystalline regions are formed with the liquid alloy even at the substrate temperature of 500°C. The liquid alloy of gold--silicon, and the polycrystalline regions are

transformed to the polycrystalline gold and silicon rich regions during cooling to room temperature. Figure 10(a), 10(b), and 10(c) show the electron diffraction pattern, the morphology, and the internal features of the transformed polycrystalline gold and silicon rich regions.

The results obtained may be explained in terms of the surface atomic mobility of gold adatoms on silicon substrate and strong substrate/overgrowth reactions involving alloying and interdiffusion, especially the favorable diffusion of silicon into the gold film. In order to obtain epitaxial growth, an adatom should have sufficient time and atomic mobility to jump to an equilibrium position of an ordered state by surface diffusion. These conditions do not obtain.

At low substrate temperatures, below 200°C, quite low atomic mobility of gold adatom and strong bonding between overgrowth and substrate do not lead to strong interaction between adatoms and the favorable growth of the deposit with the substrate. Very weak interdiffusion between gold and silicon at this temperature range also makes alloying of gold and silicon difficult. A thin amorphous layer of gold is formed just by the rapid adsorption of incident gold atoms at early stages. At later stages in the deposition, the bonding between substrate and overgrowth is significantly diminished, and thus, gold adatoms may grow by the interaction with other adatoms and the capture of incident atoms. Polycrystalline gold islands grow on a newly formed amorphous layer. At the temperatures 120-200°C, the coalescence of polycrystalline gold islands due to the high mobility of adatoms and the strong bonding between substrate and overgrowth lead to the formation of the two dimensional micro-sized polycrystalline

gold islands.

In the high temperature region, above the eutectic temperature of 200°C, the atomic mobility of gold adatoms and the surface diffusivity of silicon atoms is believed to be sufficiently high to have strong substrate/overgrowth interactions. As the gold atoms are being deposited on the silicon substrate, the outermost silicon atoms interact with the gold atoms and make a liquid alloy. The extra gold or silicon atoms respectively form the polycrystalline gold or silicon rich regions. It depends on the diffusivity of silicon atoms through the liquid alloy whether the polycrystalline islands are gold rich regions or silicon rich regions. The following three factors show that the polycrystalline islands are silicon rich regions.

1. The phase diagram of a gold--silicon binary alloy in Figure 11, shows that the concentrations of the eutectic are 31 atomic per cent silicon and 69 atomic per cent gold. Above the eutectic temperature the concentration of silicon should be higher than 31 atomic per cent in order to form polycrystalline silicon rich regions inside the liquid islands. This requires the diffusivity of silicon through the liquid alloy to be higher than 1/3 the deposition rate of gold. An experiment performed by Anthony and Cline [1972]¹ shows that the effective diffusion coefficient of silicon through the gold--silicon liquid is described by

$$D = 1.6 \times 10^{-5} \text{ cm}^2/\text{sec. at } 300^\circ\text{C.}$$

It is, therefore, believed that silicon atoms diffuse through the liquid alloy 4 orders of magnitude faster than the deposition rate

of gold, resulting in the formation of the polycrystalline silicon rich regions.

2. The lattice constant obtained from the electron diffraction pattern of the polycrystalline rings of the alloy is nearly the same as that of silicon. The gold d value is $4.0783 \text{ \AA}^\circ$ and the silicon d value is $5.4282 \text{ \AA}^\circ$.

3. Liquid islands had been only obtained in vacuum of 10^{-6} torr, while liquid and polycrystalline islands have been observed in vacuum of 1×10^{-8} torr. If the polycrystalline islands are gold rich regions, much more polycrystalline gold rich regions should be obtained in vacuum of 10^{-6} torr since the interdiffusion between gold and silicon is very weak due to the residual gases on the substrate. This makes the hypothesis of the polycrystalline gold rich regions rather weak.

The data obtained in vacuum of 1×10^{-8} torr have shown two major discrepancies with the data² obtained in vacuum of 10^{-6} torr.

1. At low substrate temperatures, below 200°C , three dimensional polycrystalline gold islands had been obtained in vacuum of 10^{-6} torr (Figure 12(a)), while two dimensional polycrystalline gold islands are obtained in vacuum of 1×10^{-8} torr (Figure 12(b)).

2. At high substrate temperatures, above 200°C , a liquid alloy of gold--silicon has been obtained only in a vacuum of 10^{-6} torr (Figure 13(a)), while the liquid alloy of gold--silicon, and the polycrystalline silicon rich regions have been obtained in vacuum of 1×10^{-8} torr (Figure 13(c)).

Both cases may be explained in terms of the effect of residual gases on the thin film growth kinetics. In vacuum of 10^{-6} torr,

there is a substantial component of hydrocarbon vapors in the residual gases due to the large number of o-ring seals, vacuum greases and pump oils. An equilibrium distribution of adsorbed gas molecules exists on a substrate surface during deposition under these vacuum conditions since the flux of residual gas atoms are impinging on the substrate surface is equivalent to one monolayer per second³. Deteriorations of the bonding and interdiffusion between overgrowth and substrate due to the residual gases on the substrates, and the interaction between the gas atoms with the electron beam and the substrate give rise to the growth of the three dimensional polycrystalline gold islands at low substrate temperatures, and the formation of only the liquid alloy of silicon--gold at high substrate temperatures.

In vacuum of 1×10^{-8} torr, the flux of residual gas atoms impinging on the substrate surface is equivalent to 4×10^{-3} monolayers/sec³, which is far below the deposition rate of the gold atoms. (It takes about 5 min to form a monolayer of residual gases on the substrate). It is therefore concluded that the residual gases under these vacuum conditions do not have much effect upon the nucleation and growth kinetics of sputtered thin films.

The electron irradiated area was compared with other substrate areas during the deposition process and after deposition was terminated in order for determining in an in situ experiment the effect of the electron beam.

It was found that a larger number of polycrystalline gold islands were grown in the irradiated area (Figure 14(a)) than nonirradiated area (Figure 14(b)) at 152°C substrate temperature, and faster growth and earlier coalescence of the deposited islands

in the irradiated area (Figure 15(a)) resulted in the formation of the islands of larger size than that in the non-irradiated area (Figure 15(b)), at 300°C substrate temperature. The substrate was heated up to 350°C and then cooled down to the room temperature after the deposition was terminated at 152°C substrate temperature. A comparison of Figure 14(c) and 14(d) shows that the electron beam damage to the substrate results in a great number of preferential nucleation sites, resulting in more intense polycrystalline gold ring pattern.

Review of Epitaxial Growth and Structure of CdS Films

Usually CdS crystallizes in two basic crystal modifications: the hexagonal wurtzite structure and the cubic sphalerite structure. These are shown in Figure 16.

Epitaxial growth and structure of CdS films⁴⁻⁵ may mainly be influenced by substrate orientation and substrate temperature. They may also be influenced by contamination, defects, deposition rate, and annealing.

Substrate Orientation. The single crystal substrate has a dominant influence on the oriented growth and structure of the deposit. Epitaxy can occur between two substances of completely different types of chemical bonds. Some symmetry exists, though not always obvious, between the contacting planes of the two materials. The symmetry relation may be produced by generalized translation and/or rotational movements of the two lattices. Symmetry considerations bearing on deposit/substrate interfacial energies ensure that the material forms with the substrate structure for low temperature growth.

Substrate Temperature. Substrate temperature is an important factor determining the structure on differently oriented substrates. The influence of the substrate orientation outlined above predominates only for low temperature growth. At high temperatures sufficient thermal energy is available to permit phase transformations to a lower energy structure to take place even if the higher energy structure should tend to form first.

Contamination and Defects. A substrate surface is intrinsically inhomogeneous due to the existence of contamination and defects, which create locally a strong interfacial interaction on the substrate surface. At these local spots, nucleation occurs preferentially. Since the interfacial interaction at locations other than such local spots remains weak, growth still occurs with the distinct characteristics of weak interfacial interaction.

Deposition Rate. For epitaxy, an adatom should have sufficient time to jump to an equilibrium position of an ordered state by surface diffusion before it interacts with another adatom. For a given system with fixed atomic mobility, this is satisfied if the deposition rate of monolayer should be less than the jump frequency of adatoms. At sufficiently high deposition rate, adatoms easily interact with each other and form stable nuclei. Thus, increasing the deposition rate yields a larger number of initial nuclei of smaller size, resulting in a higher rate of formation for smaller islands and in an earlier coalescence. However, increasing the deposition rate may decrease the structural perfection of the films considerably since an adatom does not have sufficient time to jump to an equilibrium position of an ordered state.

Annealing. Single crystal films obtained by vapor deposition usually include a high density of imperfections. However, small particles at the initial stage of deposition are found to be essentially defect free before they coalesce. These defects may be introduced during the coalescence process. The density of dislocations steadily increases as the average film thickness increases and the largest increase occurs at the channel and hole stage of the film formation just before the continuous film is formed. Most dislocations would be introduced due to the existence of displacements and rotations between neighboring nuclei at the coalescence when a hole remains before it is completely filled. Annealing treatments can improve considerably the perfection of evaporated films. The number of dislocations is reduced significantly and further recrystallization occurs in many cases, especially that of films deposited at low temperatures.

Conclusions

The study of in situ ion beam sputtering of gold on substrates of single crystal silicon shows that substrate/overgrowth interaction greatly influences the growth and structure of the deposits. At temperatures below 200°C, the strong bonding and weak interdiffusion between substrate and overgrowth results in the formation of an initial amorphous layer followed by the growth of two dimensional polycrystalline gold islands with increased film thickness. At substrate temperatures above 200°C, strong substrate/overgrowth interactions lead to the formation of a liquid alloy of gold--silicon rather than the epitaxial growth of gold films with the substrate of silicon. The polycrystalline silicon rich regions are

formed inside the liquid alloy due to the diffusion of silicon through the liquid alloy 4 orders of magnitude faster than the deposition rate of gold.

The residual gases on the substrate have a significant effect upon the growth and structure of sputtered thin films. Deteriorations of the bonding and interdiffusion between overgrowth and substrate due to the residual gases, and the interactions between the gas atoms with the electron beam and the substrate give rise to the growth with the distinct characteristics of true substrate/overgrowth interaction.

The formation of a great number of preferential nucleation sites on an irradiated area due to the electron beam damage gives rise to the growth of polycrystalline gold islands from very early in the growth process, while inhibiting the early coalescence of the islands at temperatures below 200°C. In the high temperature region above 200°C, the thermal energy due to the high energy electron beam leads to faster growth and earlier coalescence of the deposited islands, resulting in the formation of the islands of smaller number of larger size.

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Figure Captions

- Figure 1: Ultrahigh vacuum in situ deposition system.
- Figure 2: Gross section of hot stage assembly and apertures of ultrahigh vacuum specimen chamber.
- Figure 3: Specimen heater cone and thermocouple of ultrahigh vacuum chamber hot stage assembly.
- Figure 4: Schematic of ultrahigh vacuum in situ deposition system.
- Figure 5: Mass spectrums obtained from the quadrupole mass spectrometer:
- (a) before introducing liquid nitrogen into the reservoir (chamber cold ring);
 - (b) after introducing liquid nitrogen into the reservoir; and
 - (c) after opening the argon leak valve.
- Figure 6: Series of electron diffraction patterns depicting the growth and transformation of gold on silicon. Substrate temperature (T) = 152°C. Deposition rate = 15 Å/min.
- (a) Formation of an amorphous layer of gold on silicon at 400 sec. deposition time.
 - (b) The growth of polycrystalline gold islands on a newly formed amorphous layer at 1450 sec.
 - (c) A liquid alloy of gold--silicon obtained from polycrystalline gold islands after the deposits

in Figure 6(b) had been heated up to 350°C.

(d) Polycrystalline gold obtained after the liquid alloy in Figure 6(c) had been cooled down to room temperature.

Figure 7: Series of micrographs depicting the growth of gold on silicon. $T = 152^{\circ}\text{C}$, Deposition rate = $15 \text{ \AA}^{\circ}/\text{min}$. (a) 210 sec.; (b) 1005 sec.; (c) 2064 sec.

Figure 8: Growth sequence of gold on silicon. $T = 300^{\circ}\text{C}$, Deposition rate = $15 \text{ \AA}^{\circ}/\text{min}$. (a) 208 sec.; (b) 235 sec.; (c) 290 sec.; (d) 498 sec.; (e) 539 sec.; (f) 576 sec.; (g) 1299 sec.; (h) 1663 sec.; (i) 2235 sec.

Figure 9: Series of electron diffraction patterns depicting the growth of liquid alloy of gold--silicon, and polycrystalline silicon rich regions. $T = 504^{\circ}\text{C}$, Deposition rate = $15 \text{ \AA}^{\circ}/\text{min}$. (a) 417 sec.; (b) 716 sec.; (c) 1286 sec.

Figure 10: (a) electron diffraction pattern, (b) morphology, and (c) internal features of polycrystalline gold and silicon rich regions obtained from liquid alloy and polycrystalline silicon after the deposits in Figure 9 had been cooled down to room temperature.

Figure 11: Phase diagram of gold--silicon binary alloy.

Figure 12: Comparison of morphologies of gold deposited on silicon in the low temperature region under different

vacuum conditions.

- (a) Three dimensional polycrystalline gold islands obtained in vacuum of 10^{-6} torr. $T = 200^{\circ}\text{C}$, Deposition rate = 20 Å/min. Deposition time = 1500 sec.
- (b) Two dimensional polycrystalline gold islands obtained in vacuum of 1×10^{-8} torr. $T = 152^{\circ}\text{C}$. Deposition rate = 15 Å/min. Deposition time = 1903 sec.

Figure 13: Comparison of electron diffraction patterns of the deposits obtained in the high temperature region under different vacuum conditions.

- (a) Electron diffraction pattern of liquid alloy of gold--silicon obtained in vacuum of 10^{-6} torr. $T = 505^{\circ}\text{C}$.
- (b) Electron diffraction pattern of polycrystalline gold obtained from liquid alloy after the deposits in Figure 13 (a) had been cooled down to room temperature.
- (c) Electron diffraction pattern of liquid alloy of gold--silicon and polycrystalline silicon obtained in vacuum of 1×10^{-8} torr. $T = 504^{\circ}\text{C}$.
- (d) Electron diffraction pattern of polycrystalline gold and silicon obtained from liquid alloy and polycrystalline silicon after the deposits in Figure 13 (c) had been cooled down to room temperature.

Figure 14: Comparison of electron-irradiated and non-irradiated areas during deposition of gold on silicon in the low temperature region, below 200°C. $T = 152^{\circ}\text{C}$, Deposition rate = 15 Å/min.

- (a) Electron irradiated area at 2064 sec.
- (b) Electron non-irradiated area at 1903 sec.
After deposition carried out at 152°C, the substrate was heated up to 350°C and then cooled to room temperature.
- (c) Micrograph and electron diffraction pattern of electron irradiated area.
- (d) Micrograph and electron diffraction pattern of electron non-irradiated area.

Figure 15: Comparison of electron-irradiated and non-irradiated areas during deposition of gold on silicon in the high temperature region. $T = 300^{\circ}\text{C}$, Deposition rate = 15 Å/min.

- (a) Electron irradiated area at 1663 sec.
- (b) Electron non-irradiated area at 1796 sec.

Figure 16: (a) Wurtzite structure. This is really the sphalerite structure with the anion sites in an HCP lattice rather than the FCC of sphalerite.

(b) Sphalerite structure. The anion lattice is FCC, with anions in all the upright tetrahedra.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

(a)

(b)

(c)

(d)

Figure 6

(a)

(b)

(c)

0.5 μ

Figure 7

(a)

(b)

(c)

0.3 μ
|-----|

Figure 8

(a)

(e)

(f)

0.3μ

(g)

(h)

(i)

0.3 μ
|-----|

(a)

(b)

(c)

Figure 9

(a)

(b)

(c)

Figure 10

0.2 μ

Figure 11 Au-Si

(a)

(b)

Figure 12

0.5 μ

(a)

(b)

(c)

(d)

Figure 13

(a)

(b)

(c)

(d)

Figure 14

0.5 μ
|-----|

(a)

(b)

Figure 15

0.5 μ
|-----|

(a) Wurzite structure

(b) Sphalerite structure

Figure 16