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Contract No. AFOSR-91-0220 Growth and Structure of MBE-Deposited Iridium Silicide Technical Contact: Lt. Col. Gernot S. Pomrenke

Charles M. Falco, P.I. Arizona Research Laboratories University of Arizona Tucson, AZ 85721

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ABSTRACT

This report describes accomplishments made during the previous three years on a research program to prepare iridium silicide films by Molecular Beam Epitaxy—MBE, and characterize their physical and chemical structure in detail as a function of preparation conditions using the wide variety of probes available in our laboratory. By use of our MBE growth techniques we were able to form pure IrSi₃ films at temperatures as low as 450 °C, which is almost 200 °C lower than previously reported. We also found a previously-unreported c-axis epitaxial IrSi₃ growth mode at ~700 °C, found that the IrSi₃ epitaxy on Si(111) was dominated by a Mode B* orientation which had not previously been reported in the literature, as well as showed that the epitaxial growth of IrSi₃ on Si(111) was superior to that on Si(100). Measurements made at Rome Laboratory found that the Schottky barrier height of the IrSi₃ film on Si(111) was considerably larger than that on Si(100) substrates. We also studied in detail the growth and structure of five different types of iridium silicide films: co-deposited IrSi₄, reacted IrSi_x, co-deposited IrSi₃, and pure Ir reacted on hot Si substrates. This allowed us to form a previously-unreported silicide, Ir₃Si₄, and identify six epitaxial growth modes of Ir₃Si₄ crystallites with the Si(100) surface.

GROWTH AND CHARACTERIZATION RESULTS FOR IRIDIUM SILICIDES

L Introduction

One of the most serious problems in the growth of iridium silicide is achieving high quality silicon-silicide interfaces. Thus, in addition to depositing the materials under highlycontrolled conditions, detailed characterization of the samples produced as part of this research program was essential. For example, information is required with better than a few

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Ångstroms resolution about the structure, interdiffusion, sharpness, chemical purity, and electronic properties of the interfaces. Given the importance of this problem, it is necessary to have techniques for determining details of the composition profile at the interfaces (i.e. distance of interdiffusion, roughness, presence of oxides or intermetallic compounds, etc.). The *in situ* analysis techniques we have as part of our MBE systems (XPS, ion mill Auger, and ISS) had the necessary sensitivity and depth resolution for the composition analysis of the iridium silicide surfaces we prepared over the past three years. Also, we used RHEED to determine the crystalline symmetry of the surface of the silicide films, and LEED for quantitative determination of the surface and interface atomic positions. Cross-sectional TEM studies provided both the required near-atomic-resolution images as well as microdiffraction patterns from the interfacial regions, and Atomic Force Microscopy (AFM) determined the surface roughness with equivalent resolution.

II. Summary of Our Most Significant Results

We used Molecular Beam Epitaxy over the past three years to study the growth of IrSi₃ films on Si(100) and Si(111) substrates. We initially studied IrSi₃ produced by codepositing Ir and Si in a 1:3 atomic stoichiometry to aid in the formation of pure, single phase films. We chose IrSi3 due to its reported high barrier height on n-type Si(100) which would, therefore, provide a very low barrier height on p-type Si(100). We studied films of both 450 Å and 100 Å thickness. The relatively thick 450 Å films allowed us to obtain accurate x-ray characterization of the IrSi3 film growth as well as detection of other iridium silicide phases if they were present. We used Seemann-Bohlin x-ray diffraction, which is sensitive to the randomly oriented grains in these films, to determine the phase of our polycrystalline samples. We found pure IrSi₃ films could be formed at temperatures as low as 450 °C, which is almost 200 °C lower than previously reported, on both Si(100) and Si(111) substrates. A typical IrSi₃ spectrum from a 100 Å IrSi₃ film deposited at 550 °C is shown indexed in Figure 1. Transmission Electron Diffraction (TED) verified the purity of these IrSi3 films. In Figure 2 we show a TED image from a 100 Å sample deposited at 530 °C, which we have indexed as corresponding to IrSi₃. The ring-like pattern in this figure is consistent with polycrystalline growth.

Bragg-Brentano x-ray diffraction, which is sensitive only to planes which are parallel to the substrate surface, allowed us to determine possible epitaxial growth modes as a

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Figure 1. Seemann-Bohlin spectrum from a 100 Å sample deposited on Si(100) at 550 $^{\circ}$ C showing peaks due to IrSi₃ polycrystalline film growth.



Figure 2. Transmission electron diffraction (TED) pattern showing polycrystalline rings indexed as $IrSi_3$ from a 100 Å $IrSi_3$ film on Si(111).

function of deposition temperature for our co-deposited IrSi₃ films on Si(100) and Si(111). We developed a normalization procedure which accounts for the structure and Lorentz polarization factors, and use it to deduce the relative quantities of the various possible epitaxial orientations (termed "modes" in the rest of this discussion) identified from peaks in our spectra, such as the one shown in Figure 3. In this Figure a number of possible epitaxial growth-mode orientations are identified. We found a total of seven possible modes for growth on Si(111) and three on Si(100) in our temperature study. Table 1 summarizes the orientations of the hexagonal IrSi₃ crystallites by giving the theoretical Bragg angle (2θ) for



Figure 3. Bragg-Brentano spectrum showing peaks due to c-axis oriented, mode B^{*} epitaxy found for deposition temperatures around 700 °C on Si(111) substrates. The 100 Å IrSi₃ film, deposited at 670 °C shows peaks consistent with other epitaxial modes described in Table I.

each of the orientations and a possible orientation with respect to the silicon substrate. We found that the epitaxial growth of $IrSi_3$ on Si(111) was superior to that on Si(100). Ion beam channeling confirmed this by the lower χ_{min} values given in Table 2, where χ_{min} is a ratio of reflected to incident intensity from the sample ($\chi_{min} \equiv 0$ for a perfect single crystal, and $\equiv 1$ for a polycrystalline, disordered, or amorphous sample). We found that the $IrSi_3$ epitaxy on Si(111) was dominated by the Mode B* orientation which had not previously been reported in the literature. We were able to verify the existence of this epitaxial orientation using Low Energy Electron Diffraction (LEED), Reflection High Energy Electron Diffraction (RHEED) and TED. A TED image from a 100 Å IrSi3 film deposited on Si(111) at 670 °C shown in Figure 4 confirms the registry of the crystallites with the Si(111) surface. At temperatures above 780 °C another epitaxial orientation was found to exist in large quantities, which we designate as Mode A in Table 1. The TED image shown in Figure 5 confirmed the epitaxial orientation with the Si(111) surface. We also identified in our samples the C mode of epitaxy as described in Table 1. In addition, we found epitaxial growth for $IrSi_3$ on Si(100) in samples deposited between 630 °C and 780 °C, where the orientation of the $IrSi_3[2\overline{1}\overline{1}\overline{3}]$ Si[100] and $IrSi_3[01\overline{1}0]$ Si[1 $\overline{1}0$] defines a previously unreported epitaxial growth mode for $IrSi_3$ crystallites on Si(100). We labelled this Mode K. The Mode K crystallite

Mode	Bragg Angle (20) degrees	Matching Planes	Epitaxial condition
A	41.38	IrSi ₃ (2110) Si(111)	IrSi ₃ [0001] [Si[112]
В	26.92	IrSi ₃ (0001) Si(111)	lrSi ₃ [1010] I Si[110]
B*	26.92	IrSi ₃ (0001) Si(111)	IrSi ₃ [1010] I Si[211]
С	50.21	IrSi ₃ (0221) Si(111)	IrSi ₃ [0114] [Si[121]
D	47.70	IrSi ₃ (1013) I Si(111)	IrSi ₃ [1210] I Si[112]
E	23.54	IrSi ₃ (1010) Si(111)	IrSi ₃ [1210] ISi[211]
E*	23.54	IrSi ₃ (1010) I Si(111)	IrSi ₃ [1210] I Si[110]
F	36.05	IrSi ₃ (1012) Si(111)	IrSi ₃ [1210] I Si[211]
G	27.16	IrSi ₃ (1011) [Si(111)	IrSi ₃ [1210] Si[211]
Н	26.92	IrSi(0001) I Si(100)	IrSi ₃ [1010] Si[110]
1	23.54	IrSi(1010) ISi(100)	IrSi ₃ [0001] Si[010]
*	23.54	IrSi(1010) ISi(100)	IrSi ₃ [0001] Si[011]
J	27.16	IrSi(0111) ISi(100)	IrSi3[0112][Si[110]

Table I. Table describing peaks seen in Bragg-Brentano spectra on $IrSi_3$ films and possible epitaxial orientations with the silicon substrate.

Substrate orientation	Deposition Temperature	χ _{min} of Ir in film	Substrate orientation	Deposition Temperature	χ _{min} of Ir in film
Si(100)	530 °C	0.95	Si(111)	580°C	0.94
Si(100)	630 °C	0.92	Si(111)	680 °C	0.66
Si(100)	680 °C	0.92	Si(111)	730 °C	0.64
Si(100)	730 °C	0.89	Si(111)	780 °C	0.84
Si(100)	780 °C	0.93	Si(111)	830 °C	0.65

Table II. Ion beam channeling results showing better epitaxial quality on Si(111) by the lower χ_{min} values for these films compared to similar depositions on Si(100).

orientation does not produce a matching plane with the Si(100) surface. The (hkil) index of this plane is irrational, explaining why no evidence of this epitaxial growth is identified by Bragg-Brentano analysis.



Figure 4. TED pattern of Mode B* oriented crystallites.



Figure 5. TED pattern of Mode A oriented crystallites.

We fabricated a shadow mask from Mo with a number of 1/16" diameter diode areas for characterization of these films as infrared photodetectors. Measurements made at Rome Laboratory showed that the Schottky barrier height of the IrSi₃ film on Si(111) was considerably larger than that on Si(100) substrates. Figures 6 and 7 show the photoresponse plots for a 100 Å IrSi₃ film on Si(111) and a 50 Å film on Si(100). Unfortunately, the barrier heights found for $IrSi_3$ on Si(111) of around 0.33 eV and on Si(100) of 0.175 eV would not allow imaging in the Long Wavelength InfraRed (LWIR) of 8–12 µm. Detection of photons in this region requires barrier heights lower than 0.155 eV. However, a device with a barrier height of 0.175 eV could be useful in the Medium Wavelength InfraRed (MWIR) of 3–5.4 µm where PtSi detectors now are generally used. This would be of great value if the performance in the 4.5–5.4 µm window could be made greater than a PtSi detector. Studies involving tuning the thickness and deposition temperature of this material to provide maximum emission efficiency would be required to explore this possibility.



Figure 6. Fowler plot from a 100 Å $IrSi_3$ film deposited on Si(111) at 530 °C. The barrier height of 0.33 eV corresponds to a 3.7 µm cutoff.



Figure 7. Fowler plot from a 50 Å IrSi₃ film deposited on Si(100) at 450 °C. The cutoff wavelength of the detector is beyond 7 μ m.

We also studied the growth and structure of five different types of iridium silicide films: codeposited and reacted IrSi, codeposited Ir₃Si₄, reacted IrSi, codeposited IrSi, and

pure Ir reacted on hot Si substrates. A comparison of the Seemann-Bohlin x-ray spectra found for polycrystalline formation of these iridium silicide films is given in Figure 8. The spectrum from each film type is unique. With TED we were able to verify that these films are different in structure. This can be seen from a comparison of the TED patterns of an Ir_3Si_4 film (Figure 9) to that of an IrSi film (Figure 10). These films were deposited at room temperature and annealed at 450 °C for 1 hour. Atomic Force Microscopy (AFM) shows the surface of the Ir_3Si_4 film to be much smoother than the similarly processed IrSi film. The AFM measurements of the Ir_3Si_4 film showed a 3 Å RMS roughness and of the IrSi film a 12 Å RMS roughness. Both samples contained ~50 Å of iridium. We confirmed the smooth surface of the Ir_3Si_4 film using Transmission Electron Microscopy (TEM) on a cross section of the above film.



Figure 8. Seemann-Bohlin spectra from four unique iridium silicide films showing clear differences in their characteristic peak positions.



Figure 9. TED from an Ir_3Si_4 film deposited at ambient and reacted at 450 °C to form a silicide.



Figure 10. TED pattern characteristic of IrSi phase, for a film co-deposited at ambient and annealed to 450 °C.

We found that Ir_3Si_4 co-depositions on Si(100) at temperatures between 450 °C and 550 °C form localized epitaxial films. Figure 11 shows the TED pattern from a film codeposited at ~500 °C. The pattern shows the presence of six epitaxial growth modes of Ir_3Si_4 crystallites with the Si(100) surface, where the primed indexing refers to a 90 degree rotation on the Si(100) surface of the same crystallite orientation. A description of these epitaxial growth modes is as follows;

Ir ₃ Si ₄ [102] Si[001]	Ir ₃ Si ₄ (402) Si(022)
Ir ₃ Si ₄ [102] Si[001]	Ir ₃ Si₄(402)∥Si(022)
Ir ₃ Si ₄ [203] Si[001]	Ir ₃ Si ₄ (302) Si(022)
Ir ₃ Si ₄ [203] Si[001]	Ir ₃ Si ₄ (302) Si(022)
Ir ₃ Si ₄ [201] Si[001]	Ir ₃ Si ₄ (102) Si(022)
Ir ₃ Si ₄ [201] Si[001]	Ir ₃ Si ₄ (102) Si(022)
	$ \begin{split} & \operatorname{Ir}_3\operatorname{Si}_4[102] \ \operatorname{Si}[001] \\ & \operatorname{Ir}_3\operatorname{Si}_4[102] \ \operatorname{Si}[001] \\ & \operatorname{Ir}_3\operatorname{Si}_4[203] \ \operatorname{Si}[001] \\ & \operatorname{Ir}_3\operatorname{Si}_4[203] \ \operatorname{Si}[001] \\ & \operatorname{Ir}_3\operatorname{Si}_4[201] \ \operatorname{Si}[001] \\ & \operatorname{Ir}_3\operatorname{Si}_4[201] \ \operatorname{Si}[001] \\ \end{split} $

We found the Ir_3Si_4 films formed by annealed reactions are polycrystalline in structure on both Si(100) and Si(111) substrates. Figure 9 shows the electron diffraction pattern from an Ir_3Si_4 film annealed at 450 °C. The randomly distributed spots located in the pattern are consistent with the lack of epitaxial growth in this film. We observed similar diffraction patterns on both Si(100) and Si(111) substrates for annealing temperatures of 450 °C and 550 °C. The d-spacings measured from the diffraction patterns of these polycrystalline films are consistent with the Ir_3Si_4 crystal structure.



Figure 11. TED pattern from a film codeposited at ~500 °C. The pattern shows the presence of six epitaxial growth modes of Ir_3Si_4 crystallites with the Si(100) surface.

Measurement made at Hanscom AFB of an Ir_3Si_4 film deposited on a hot silicon substrate at 450 °C revealed fairly good infrared detector characteristics as shown in Figure 12. The C₁ value of > 9 %/eV and cutoff wavelength in the LWIR of 8.9 µm shows promise for LWIR detectors to be developed from this film type. Measurements also were made at Hanscom AFB on our annealed Ir_3Si_4 films. The data from these films showed slightly lower barrier heights out to ~10 µm. However, they displayed lower C₁ values than that of the hot-

deposited film.



Figure 12. Fowler plot for an Ir_3Si_4 film at 450 °C showing photoresponse out to nearly 9.0 µm. The C₁ coefficient of > 9 %/eV is very high for an iridium silicide film.

We also studied silicide formation for Ir films deposited on hot Si substrates at ~500 °C. From peaks observed in x-ray diffraction, we were able to confirm Ir₃Si₄ growth in these reactions. TED confirmed that the Ir₃Si₄ films formed by Ir depositions at 500 °C contain epitaxial Ir₃Si₄ growth. The electron diffraction patterns (similar to Figure 11) clearly showed the formation of the Ir₃Si₄ A, B, and C localized epitaxial growth modes on Si(100) as described above. The TED pattern in Figure 13 displayed the highly oriented Ir₃Si₄ crystallite growth formed by depositing Ir on Si(111) at 500 °C. The relatively sharp diffraction spots observed in the pattern are due to localized epitaxial growth of Ir₃Si₄ crystallites on the Si(111) surface having a three-fold degeneracy. We labeled these Ir₃Si₄ epitaxial growth modes, Mode D, D', and D" as follows:

Mode D	Ir ₃ Si ₄ (100) Si(111)	Ir₃Si₄[010]∥Si[110]
Mode D'	Ir ₃ Si ₄ (100) Si(111)	Ir₃Si₄[010]∥Si[101̄]
Mode D''	Ir ₃ Si ₄ (100) Si(111)	Ir ₃ Si ₄ [010] Si[110]



Figure 13 . TED pattern displaying the highly oriented Ir_3Si_4 crystallite growth formed by depositing Ir on Si(111) at 500 °C.

Mode D epitaxial growth establishes the fact that the $Ir_3Si_4(100)$ plane is parallel to the Si(111) surface, and is consistent with the diffraction peaks of the $Ir_3Si_4(800)$ and $Ir_3Si_4(14,00)$ planes,

which we observed in the Bragg-Brentano spectra of these films.

We made measurements of the electrical properties of our iridium silicide films using the 1/16" diodes discussed above. By measuring the current at a fixed reverse bias voltage on the diode (0.1 to 1.0 volt) we obtained the thermal barrier height of the device by plotting $ln(I/T^2)$ vs. $1/k_BT$. Here I is the current measured, T is the temperature of the device, and k_B is Boltzman's constant. We measured an extremely low barrier height of 0.1 eV for an Ir_3Si_4 sample which was deposited at ambient and subsequently annealed to 500°C. The value of the barrier height is derived by the slope of the plot in the linear region of Figure 14.



Figure 14. Activation energy plot used to derive a 0.10 eV thermal barrier height from an Ir_3Si_4 film codeposited at ambient and annealed to 500 °C.

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6.

Quantitative Analysis of Bragg-Brentano Data for Highly-Oriented Thin-Film Samples. Gary A. Gibson, D. A. Lange and Charles M. Falco, J. Appl. Phys - SUBMITTED.

STUDENTS AND POSTDOCS WORKING ON THIS CONTRACT

Dr. Gary Gibson worked on this contract for its first two years. He left in the Spring of 1993 to take a full-time position as member of the technical staff at Hewlett-Packard Research Laboratories in Palo Alto.

Davis Lange has been working on this contract for the full three years, as part of his Ph.D. dissertation research. I expect him to receive his Ph.D. within a year from now.