

MBE GROWTH OF METAL/SEMICONDUCTOR INTERFACES

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INTRODUCTION

Metal/semiconductor structures are of interest in several fields including thin-film magnetism, electronics, and x-ray optics. Well controlled and characterized interfaces are crucial for the understanding of the properties of nanostructured materials. We describe techniques used to grow and characterize three such material systems: Co/Pd on GaAs(110) (using a bcc-Co seed layer), Co on Si(111), and Mo on Si(111).

The Co/Pd system is of interest for its magnetic and magneto-optic properties. In particular, several workers have observed polarization of the Pd in Co/Pd multilayers¹ as well as a strong perpendicular magnetic anisotropy.² We have grown epitaxial Co/Pd superlattices on GaAs(110) substrates by first depositing a suitable buffer layer of Pd. The growth of the Pd buffer layer and the behavior of Co deposited upon it are discussed in the present paper. Structural and magnetic properties of the superlattices are discussed elsewhere in these proceedings.³

Heteroepitaxy of a variety of pure metals on GaAs has been achieved by various workers. In many cases, structures with sharp interfaces as well as good atomic order have been obtained. However, in contrast to the case with GaAs, Si reacts with most metals to form silicides, making it impossible to produce epitaxial pure-metal/Si structures similar to those made on GaAs. In fact, many metals react with Si even at room temperature. Although the problems associated with pure metals are severe, Co and several other metals (e.g. Ni and Mo) form epitaxial silicides with proper treatment. MBE techniques can then be used to form high quality epitaxial silicide/silicon multilayer structures. In the second half of this paper we discuss such techniques and their application to the growth of Co and Mo on Si(111).

GROWTH OF Co/Pd ON GaAs

The evaporations were performed in a Perkin-Elmer 433-S MBE system⁴ which was specifically designed for growth of Si and refractory metals. The Pd was evaporated from a high-temperature Knudsen cell and the Co was electron-beam evaporated. Deposition rates were 0.25 Å/s and 0.15 Å/s for Co and Pd respectively. The base pressure was 5×10^{-11} torr, and the pressure during deposition was typically 1×10^{-9} torr, with H₂ making up 70% of that total. The Co deposition rate was held constant by active feedback from an Inficon Sentinel III deposition controller⁵ which uses an electron impact emission spectroscopy

monitor to measure the flux. The substrate temperature is controlled with a feedback stabilized graphite heater, enabling temperatures as high as 1100 C to be reached when desired. Reflection high energy diffraction (RHEED) and low energy electron diffraction (LEED) are available in the growth chamber. The sample is in the growth position for RHEED but must be moved for LEED. Figure 1 shows a series of RHEED patterns taken at different stages during the depositions.

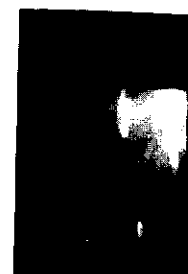
The GaAs(110) substrates were first heated to ~ 625 C for ~ 30 min to desorb the oxide from the surface. The RHEED pattern after this heating procedure is shown in Figure 1. A seed layer of Co (6 \AA) was then deposited at room temperature to begin the growth. The one attempt made to grow the Pd directly on the GaAs yielded a Pd layer which was rough and disordered compared to those grown on top of a Co seed layer. The seed layer is epitaxial bcc-Co in agreement with previous work.⁶ The RHEED and LEED patterns both indicate that, although 6 \AA of Co was deposited, it is rough and may not form a continuous layer.

A high quality Pd(111) layer was formed by deposition onto the 6 \AA Co seed layer at room temperature. Depositing additional Pd with the sample heated to 200 C produced a surface which was better still. Interestingly, the RHEED pattern degrades at the beginning of the Pd deposition. However, after deposition of $\sim 20 \text{ \AA}$ of Pd, the pattern begins to recover, indicating healing of the surface roughness. In addition, there is a "rotation" of the Pd with respect to the substrate. The bottom left photo in Figure 1 shows the RHEED pattern for the Pd surface formed by the deposition of 300 \AA of Pd at room temperature. The "rotation" of the Pd $[211]$ axis with respect to the GaAs $[111]$ axis is apparent in this figure. Continuing the deposition at 200 C produced a sharper RHEED pattern as shown. However, depositing the entire Pd layer at 200 C resulted in a poor quality (three-dimensional) surface. The final photo of Figure 1 shows the same Pd RHEED with the sample rotated slightly to center the pattern.

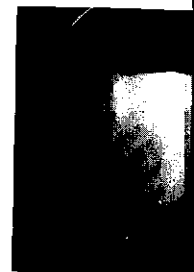
The angle of the Pd $[211]$ with respect to the GaAs $[111]$ axis was measured by comparing LEED patterns from before and after the Pd deposition. Unfortunately there is a significant amount of mechanical backlash in our present substrate rotation apparatus, which made it difficult to position the sample with exactly the same orientation for each measurement. We can only say that the rotation is on the order of 5° . Future work will include improving the rotation apparatus to allow more reproducible positioning of the sample.

Finally, the growth of thin Co layers on the Pd buffer was studied. RHEED was monitored continuously during the Co deposition, and LEED was performed after the deposition of 2 \AA and 4 \AA of Co. A series of LEED patterns taken at different energies clearly shows an enlargement of the spot distances during the Co depositions. The Pd lattice constant was determined to be that of the bulk material (3.890 \AA) within the experimental uncertainty of $\sim 1\%$. The Co lattice constant was determined to be $3.80 \pm 0.04 \text{ \AA}$ after the deposition of 2 \AA of Co and $3.63 \pm 0.07 \text{ \AA}$ after 4 \AA . In comparison, the bulk lattice constant of fcc Co is 3.544 \AA . From these measurements, we infer that the thin fcc-Co layer is initially strained to match the Pd buffer layer, but rapidly relaxes toward its bulk lattice constant. It should be noted that after only ~ 1 monolayer (ML) of Co the surface has become significantly more disordered, and becomes worse with increasing Co coverage. One could argue that the Co may be growing as small bulk-like islands, giving rise to a LEED pattern which has contributions from both the bulk Pd and bulk Co to form broad shifted spots. However, there is some evidence against this Co island interpretation from our x-ray diffraction data of Co/Pd multilayers. Since multilayers with 1 ML thick Co layers show high-angle satellite peaks and a low-angle Bragg peak, it is unlikely that the Co is forming islands.

Plans for future work includes a study of the behavior of the magnetic anisotropy in thin Co films as a function of the Co strain.



GaAs(110)



300 Å Pd

Figure 1. RHEED patterns taken at different stages during the depositions. The electron beam is incident from the left.

Co AND Mo ON Pd

Both Co and Mo (1.2% and 4.1% respectively) have been successfully deposited on Si without the formation of pinholes or, at worst, small voids. Interfaces can be formed by an anneal to ~ 500 C. CoSi₂ and MoSi₂ layers are formed.

A high-temperature anneal to desorb the native oxide indicates that the native oxide is removed. Auger spectra show that the Co and Mo deposited at $T < 1000$ C where $400 \text{ C} \leq T_{\text{high}}$ during heating of the sample. Co reacts at the low temperature background intensity with those expected for $T \approx 300 - 350$ C only a slight trace of a surface oxide.

Mo forms a silicide at low temperature.

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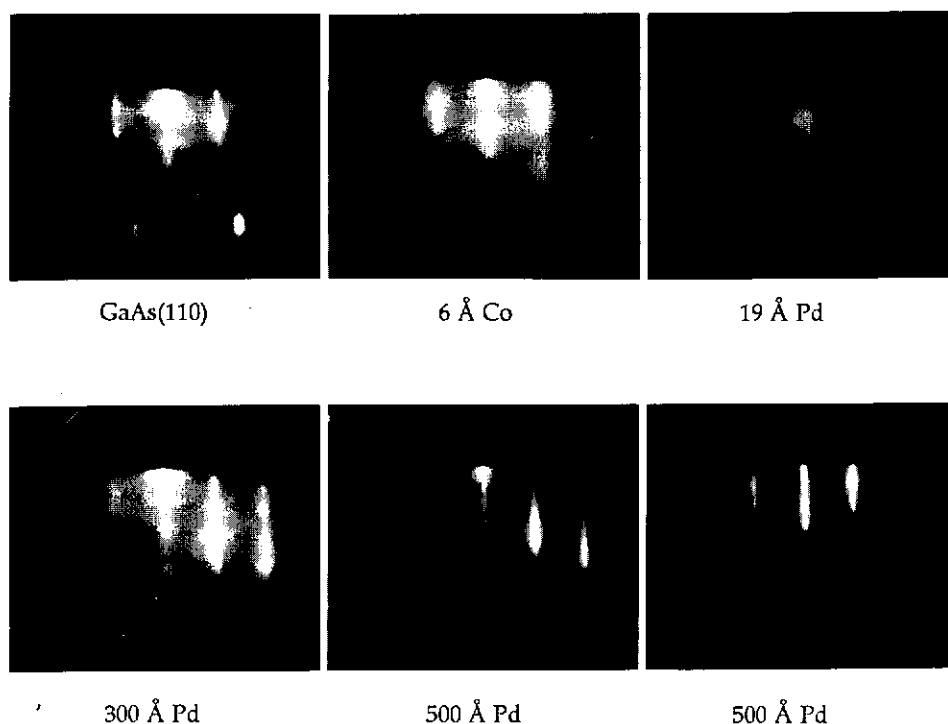


Figure 1. RHEED patterns for various stages during the growth of Pd/Co on GaAs(110). The electron beam energy was 10 Kev.

Co AND Mo ON Si(111)

Both Co and Mo form metallic disilicides which have a small lattice mismatch with Si (1.2% and 4.1% mismatch for CoSi_2 and MoSi_2 respectively).⁷ Epitaxy of CoSi_2 and MoSi_2 on Si have been studied extensively, revealing some common problems. In either case, deposition of the metal directly onto a hot Si substrate results in epitaxial films with, at best, pinholes or, at worst, large islands. Recent studies have shown that high quality CoSi_2/Si interfaces can be formed by depositing a thin (<10 Å) metal layer at $T < 100$ C followed by an anneal to ~ 500 C.⁸ In the present work, we have studied the formation of thin epitaxial CoSi_2 and MoSi_2 layers.

A high-temperature substrate heater was used to heat the Si(111) substrates to 900 C to desorb the native oxide. A buffer layer of pure Si was then deposited at 800 C. RHEED indicates that the resulting surface exhibits the well known 7×7 reconstruction, and the Auger spectra show no surface contamination. A thin layer of metal (Co or Mo) was then deposited at $T < 100$ C, following which the temperature was raised at 15 C/min. to T_{high} where $400 \text{ C} \leq T_{\text{high}} \leq 600 \text{ C}$. Analyzing the evolution of the RHEED and LEED patterns during heating of ~ 1 ML of Co on Si(111) reveals the following sequence of events. The Co reacts at the low temperature to form a disordered layer, as indicated by the high background intensity in RHEED and LEED. The diffraction patterns are dim but consistent with those expected for CoSi_2 . For $T \approx 140 - 300$ C two different phases of CoSi_2 are present, for $T \approx 300 - 350$ only one phase is present, and for $T > 350$ there is a dominant phase with a slight trace of a second.

Mo forms an amorphous silicide layer (diffuse RHEED and LEED patterns) at the low temperature. Peak shifts in the Si-2p and Mo-3d x-ray photoelectron spectroscopy

(XPS) spectra indicate silicide formation at the Mo/Si interface for growth temperatures as low as 50 C (the lowest temperature studied). The energy shift observed here is in the opposite direction from that which we have observed in well-annealed films which formed crystalline MoSi₂. This is a strong indication that the amorphous silicide which forms at 50 C and 200 C is not MoSi₂. Annealing to T_{high} = 500 - 600 C produces an epitaxial single-crystal MoSi₂ film. However, for layers with more than ~6 Å of Mo, the diffraction patterns quickly disappear. Even for the thinner layers, the MoSi₂ films are more disordered than the equivalent CoSi₂. In addition, a series of growth studies involving continuous growth of multiple Mo coverages on the silicon have been performed. The data analysis and experimental details of these growth studies are beyond the scope of the present paper, and will be published elsewhere. Here we have discussed only that part which is interesting for comparison to the case of Co on Si.

SUMMARY

High quality Pd(111) layers were formed by deposition, at room temperature, of a Co buffer layer on GaAs(110) followed by the Pd. This surface was improved by depositing additional Pd with the sample heated to 200 C. The RHEED pattern degrades at the beginning of the Pd deposition and then recovers after depositing > ~20 Å of Pd. The Pd lattice constant, after depositing 300 Å, was determined to be that of the bulk material. The thin fcc-Co layer is initially strained to match the Pd buffer layer, but rapidly relaxes toward its bulk lattice constant.

Thin Co layers were shown to react with Si(111)(7X7) at room temperature and form a single-phase CoSi₂ epilayer when annealed to ~400 C. Thin Mo layers react to form an amorphous silicide layer at temperatures as low as 50 C. The MoSi₂ films are more disordered than the equivalent CoSi₂ films.

ACKNOWLEDGEMENTS

The authors thank Craig England for useful discussions. This work is supported by the Air Force Office of Scientific Research under contract AFOSR-90-0140 and the Joint Services Optics Program under contract F-49620-88-C-0009.

REFERENCES

1. F.J.A. den Broeder, H.J.G. Draaisma, H.C. Donkersloot and W.J.M. de Jonge, J. Appl. Phys. **61**, 4317 (1987).
2. P.F. Carcia, A. Suna, D.G. Onn and R. van Antwerp, Superlattices and Microstructures **1**, 101 (1985).
3. Brad N. Engel, Craig D. England, Masafumi Nakada, Robert van Leeuwen, and Charles M. Falco, these proceedings.
4. Perkin-Elmer Physical Electronics, Eden Prairie, MN, USA.
5. Inficon Leybold-Heraeus, Inc., East Syracuse, NY, USA.
6. G. A. Prinz, Phys. Rev. Lett. **54**, 1051 (1985).
7. See for example K.L. Wang and Y.C. Kao in Heteroepitaxy on Silicon, eds. J.C.C. Fan and J.M. Poate, MRS Symp. Proc. **67**, 235 (1986).
8. See for example: Raymond T. Tung in Silicon-Molecular Beam Epitaxy, vol. II, eds. Erich Kasper and John C. Bean, CRC Press, Boca Raton, FL (1988), or J. Derrien and F. Arnaud d'Avitaya, J. Vac. Sci. Technol. **A5**, 2111 (1987).