Chapter 6

LB Diffusion Barriers on Si substrate

In the previous chapter, procedure, parameters and results of different materials' monolayers deposited (using Langmuir-Blodgett technique) on SiO₂/Si substrate were described. In this chapter, procedure and results for monolayers of same materials are given but in this case monolayers are deposited over Si substrate only and not over SiO₂/Si. This time due to the absence of SiO₂, only thermal stability of the test structures was studied.

6.1 Sample Preparation

Monolayers of Co, NiO and CoNiO were deposited using LB technique over Si substrate. Three materials (Co, NiO and CoNiO) were evaluated as barrier resulting in three types of test structures:

a) Cu/Co/Si
b) Cu/NiO/Si
c) Cu/CoNiO/Si

p-type Si (100) samples were cleaned using standard RCA cleaning method. Subphase was prepared by dissolving different precursors (for different monolayers) in DI water. Precursors used along with the molarity of the prepared subphase are listed in table 5.1. LB film deposition system APEX LB-2007 DC as shown in figure 3.5 was used. Stearic acid was dissolved in chloroform (1 mg/1 ml) and spread over the subphase [1, 2]. To transfer the monolayers on to the SiO₂/Si substrate the surface pressure was kept constant at 30 mNm⁻¹ while keeping the up and down speed 5 mm/min. As results, steartes of Co, Ni and CoNiO were transferred on to the substrate. This process was repeated 10 times. A subsequent heat treatment in air at 400 °C for 1 hour results in homogeneous Co, NiO and CoNiO films. It is known that ≈ 5 monolayers of steartes are needed to form 1 monolayer of desired material [3]. Using this argument it can be stated that in the present case 10 monolayers of steartes turned out to be ≈ 2 monolayers of Co, NiO and CoNiO, which ensure the molecular thickness required for ultrathin diffusion barriers.
A 50 nm thick copper layer on the top of the structure was deposited by thermal evaporation. Thus Cu/Barrier (Co or NiO or CoNiO)/Si test structures were prepared. The samples were annealed at different temperatures starting from 100 °C up to 450 °C in vacuum of $10^{-5}$ mbar order for 30 minutes.

6.2 Results

This section presents the results obtained from different characterizations for Co, NiO and CoNiO monolayers. Results for these three types of monolayers are presented separately. First of all, results of Co monolayer as diffusion barrier are presented then those of NiO and then of CoNiO in the last.

6.2.1 Co monolayer as barrier

EDS technique was used to inspect the presence of Co in the thin deposited layer and to see the effect of post deposition annealing. Analysis was done for deposited monolayer both before and after 1 hour of annealing at 400 °C. The results are shown in figure 6.1. Figure 4.39 (a) shows the EDS pattern of Co monolayer before annealing. Peaks corresponding to Si, Co and C are visible in this pattern. Co-St consists of the compounds of Co, C and H. These results confirm the presence of Co on the surface. Figure 6.1 (b) shows the EDS spectrum of the deposited layer after annealing at 400 °C for 1 hour. As peaks corresponding to Co and Si are visible only and that of C disappeared as stearates vanished after the annealing. These results confirmed the successful deposition of Co monolayer after annealing.

Thickness of the deposited layer was measured carefully using ellipsometer and was found to be $\approx 1$ nm which ensure the molecular thickness required for ultrathin diffusion barriers.
Surface morphology of deposited Co film obtained by AFM both before and after the heat treatment is shown in figure 6.2. Figure 6.2 (a) shows the surface morphology of as deposited film. The film becomes smoother after annealing at 400 °C as shown in the figure 6.2 (b). Average roughness values were calculated using the same AFM software which were found to be 0.54 nm and 0.27 nm for the sample before annealing and after annealing respectively.
Figure 6.2 AFM image of Co layer (a) before annealing and (b) after annealing

Figure 6.3 shows the roughness profiles obtained using AFM software corresponding to the samples before annealing and after annealing. These results show that roughness was decreased by a factor of 2 after annealing. The maximum thickness can also been seen as decreasing on the Z axis of AFM images in figure 6.2.
The samples were analyzed using XRD and Four Probe setup to investigate the interaction of copper layer with underlying silicon substrate at higher temperatures. Normally in the absence of barrier the copper of the top layer starts interacting with Si at higher temperatures resulting in the formation of copper silicides which can be recognized using XRD spectrum. As the copper in the top layer starts degrading at higher temperatures, its sheet resistance also starts increasing which can be observed using four probe resistivity setup.

Table 6.1 gives the sheet resistance data of different samples annealed at different temperatures. Figure 6.4 uses the data of table 6.1 to show the sheet resistance variation of top copper layer with respect to the annealing temperature.

It is obvious from the figure 6.4 that in case of Cu/Si structure sheet resistance start increasing after 100 °C whereas in case of Cu/Co/Si structure sheet resistance remains almost constant up to 300 °C. Increase in resistance is an indication of degradation of top copper layer. This degradation of copper layer may be due to diffusion of top copper into underlying structure. So from these results it seems that Co barrier was able to stop the degradation of Cu up to 350 °C.
Table 6.1: Sheet resistance of samples annealed at different temperatures

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Sheet Resistance (Ω cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cu/Si</td>
</tr>
<tr>
<td>25</td>
<td>0.728</td>
</tr>
<tr>
<td>100</td>
<td>0.674</td>
</tr>
<tr>
<td>150</td>
<td>1.967</td>
</tr>
<tr>
<td>200</td>
<td>25.771</td>
</tr>
<tr>
<td>300</td>
<td>--</td>
</tr>
<tr>
<td>350</td>
<td>--</td>
</tr>
<tr>
<td>400</td>
<td>--</td>
</tr>
</tbody>
</table>

Figure 6.4 % Change in sheet resistance of Cu/Si and Cu/Co/Si structures
XRD patterns of Cu/Si and Cu/Co/Si structures corresponding to different annealing temperatures are shown in figure 6.5. It is clear that in case of Cu/Si structure degradation of main copper peak was observed at 150 °C and a new peak corresponding to Cu$_3$Si also appeared in the spectrum. In Cu/Co/Si structure, the spectrum remains unchanged up to 350 °C. New peak corresponding to Cu$_3$Si appeared in the spectrum at 400 °C. These results are in accordance with sheet resistivity results. In the presence of barrier the sheet resistance was unchanged up to 350 °C and up to this temperature there was no change in XRD pattern also. According to XRD pattern, interaction of Cu and Si starts at 400 °C similarly the sheet resistance also indicates the increase at this temperature. In the same way, in the structure without barrier, the Cu$_3$Si peak appears at 150 °C and sheet resistance also increases at this temperature.

**Figure 6.5 XRD patterns of test structures (a) Cu/Si and (b) Cu/Co/Si**

SEM technique was used to study the structural changes in the top copper layer after annealing at different temperatures. Figure 6.6 shows the SEM images of Cu/Si structure after annealing at different temperatures. Magnification was kept same for all the images. From figure 6.6 (a) it is clear that as deposited copper layer was quite smooth. Figure 6.6 (b) shows the formation of some microstructures on the surface of Cu/Si sample after annealing at 150 °C which indicates the degradation of top copper layer.
Figure 6.6 SEM images of (a) as deposited copper layer and (b) Cu/Si structure annealed at 150 °C

Further the SEM images of structure with Co barrier are shown in figure 6.7. The results in figure 6.7 (a) indicates that the copper layer in Cu/Co/Si structure was stable even after annealing at 350 °C as no damage to the surface is visible. In the case of Cu/Co/Si structure the degradation was observed after annealing at 400 °C as shown in figure 6.7 (b).
These results can be correlated with XRD and four probe results. XRD and four probe results showed that barrier was stable up to 350 °C. Same can be observed in SEM images, as no significant changes were observed in surface of Cu/Co/Si structure up to 350 °C. The microstructures or hillocks were seen at 150 °C and 400 °C for the Cu/Si and Cu/Co/Si structures respectively. Hence, the structure without barrier was failed at 150 °C and the structure with barrier was stable up to 350 °C.
6.2.2 NiO monolayer as barrier

The surface pressure vs area isotherm curve of the stearic acid over water subphase, containing NiSO$_4$, is as shown in this figure 6.8. The curve shows that the required pressure was attained before the deposition process started. It is also clear from the isotherm that, the molecules got packed densely as the pressure was attained because the area/molecule was decreased. The density of the molecules leads to the uniformity of the layer being transferred onto the substrate.

![Surface pressure vs area isotherm](Figure 6.8)

**Figure 6.8** Surface pressure v/s area per molecule isotherm

EDS technique was used to inspect the presence of NiO in the thin deposited layer. The results are shown in figure 6.9. The EDS was repeated for deposited monolayer both before and after annealing at 400 °C for 1 hour. EDS pattern of NiO monolayer before annealing (figure 6.9 (a)) shows the peaks corresponding to Si, O, Ni and C.
These results show the presence of Ni and O on the surface. Figure 6.9 (b) shows the EDS spectrum of the deposited layer after annealing at 400 °C for 1 hour. It is clear from the figure that stearates were vanished after the annealing as peaks corresponding to Ni and O are visible only and that of C is disappeared. These results confirmed the successful deposition of NiO monolayer after annealing.

Surface morphology of deposited NiO film obtained by AFM, both before and after the heat treatment, is shown in figure 6.10. Figure 6.10 (a) shows the surface morphology of as deposited film. The film becomes smoother after annealing at 400 °C as shown in the figure 6.10 (b).

The surface roughness of the LB deposited films was studied using AFM. The average roughness values were calculated using the AFM software and found to be 0.97 nm and 0.20 nm for the sample before and after annealing respectively. The roughness profiles obtained
using AFM are shown in figure 6.11. It is evident from the data that roughness of the film was decreased almost 5 times after annealing.

Figure 6.10 AFM image of NiO layer (a) before annealing and (b) after annealing
Variation in sheet resistance of top copper layer with respect to the annealing temperature is shown in figure 6.12. It is obvious from the figure that in case of Cu/Si structure sheet resistance start increasing at 100 °C whereas in case of Cu/NiO/Si structure sheet resistance remains almost constant up to 350 °C. Increase in resistance is an indication of degradation of top copper layer. This degradation of copper layer may be due to diffusion of top copper into underlying structure or/and reactions of copper with underlying films. So from these results it seems that NiO barrier was able to stop the degradation/interactions of Cu up to 350 °C.

XRD patterns of Cu/Si and Cu/NiO/Si structures corresponding to different annealing temperatures are shown in figure 6.13. It is clear that in case of Cu/Si structure, degradation of main copper peak was observed at 150 °C and a new peak corresponding to Cu₃Si also appeared in the spectrum. In Cu/NiO/Si structure, the spectrum remains unchanged up to 350 °C. New peak corresponding to Cu₃Si appeared in the spectrum at 400 °C. These results are in accordance with sheet resistivity results.

In the presence of NiO barrier, the sheet resistance was unchanged up to 350 °C and there was no change in XRD pattern also up to this temperature. XRD pattern confirmed that interaction of Cu and Si starts at 400 °C. Similarly, the sheet resistance results also indicated an increase at this temperature. In the same way, in the structure without barrier, the Cu₃Si peak appears at 150 °C and sheet resistance found to increases at the same temperature.
Figure 6.12 % Change in sheet resistance of Cu/Si and Cu/NiO/Si structures

Figure 6.13 XRD patterns of test structures (a) Cu/Si and (b) Cu/NiO/Si
The morphological changes in the top copper layer as a function of annealing temperature were evaluated using SEM technique. SEM images of Cu/Si test structure at different temperatures are shown in figure 6.6 which shows the failure of barrier at 150 °C. Figure 6.14 shows the SEM results of Cu/NiO/Si samples annealed at different temperatures.

Figure 6.14 SEM images of Cu/NiO/Si structure annealed at (a) 350 °C and (b) 400 °C
From figure 6.14 (a) it can be seen that the copper layer in Cu/NiO/Si structure was stable even after annealing at 350 °C. In the case of Cu/NiO/Si structure the degradation was observed after annealing at 400 °C as shown in figure 6.14 (b) in the form of microstructures formed due to the accumulation of copper or due to interaction of copper and silicon.

These results can be correlated with XRD and four probe results. The results obtained using SEM are in accordance with XRD and four probe results and confirmed that NiO barrier was thermally stable up to 350 °C. Thus NiO was stable as barrier up to 350 °C in Cu/NiO/Si structure.

6.2.3 CoNiO monolayer as barrier

Compositional characterization was done using EDS before and after annealing at 400 °C for 1 hour. The results are shown in figure 6.15. Figure 6.15 (a) shows peaks corresponding to Si, Co, Ni, O and C before annealing. CoNiO-St consists of the compounds of Co, Ni, O, C and H. Figure 6.15 (b) shows peaks corresponding to Co, Ni, O and Si only and that of C is disappeared after annealing. These results show that stearates were vanished after the annealing.

Figure 6.16 gives the elemental data related to the samples, before and after annealing. Samples were examined for element detection and scan was run over the area enclosed in the pink rectangle as shown in figure 6.16.

Compositions obtained corresponding to the figure 6.16 (a) and (b) are shown in the table 6.2. It is obvious from the data that beside the presence of Si and O, C, Co and Ni are also present in the structure. Also, no content or non-detectable amount of C was found after annealing the samples. These results confirmed the deposition of CoNiO monolayer after annealing.
Figure 6.15 EDS spectrum of (a) as deposited monolayer and (b) monolayer after heat treatment

Figure 6.16 Area selected for element detection (a) before annealing and (b) after annealing
Table 6.2: Compositions detected using EDS

<table>
<thead>
<tr>
<th>Element</th>
<th>Before Annealing</th>
<th>After Annealing</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Weight %</td>
<td>Atomic %</td>
</tr>
<tr>
<td>Si</td>
<td>91.88</td>
<td>84.35</td>
</tr>
<tr>
<td>O</td>
<td>1.99</td>
<td>3.21</td>
</tr>
<tr>
<td>Ni</td>
<td>0.32</td>
<td>0.14</td>
</tr>
<tr>
<td>Co</td>
<td>0.09</td>
<td>0.04</td>
</tr>
<tr>
<td>C</td>
<td>5.71</td>
<td>12.25</td>
</tr>
</tbody>
</table>

Surface morphology of deposited CoNiO film was obtained using NT-MDT Solver Scanning Probe Microscope in non contact mode as shown in figure 6.17. Figure 6.17 (a) shows the surface morphology of as deposited film i.e. before annealing. The film becomes smoother after annealing at 400 °C as shown in the figure 6.17 (b).

Figure 6.17 AFM image of CoNiO layer (a) before annealing (b) after annealing
The average roughness values were calculated using AFM software and were found to be 0.90 nm and 0.34 nm for the sample before annealing and after annealing respectively. Results show almost 3 times decrease in roughness after annealing. The roughness profiles corresponding to samples before and after annealing, obtained using AFM, are shown in figure 6.18.

![Figure 6.18 Roughness of CoNiO monolayer (a) before annealing and (b) after annealing](image)

Four probe measurement results are shown in figure 6.19. Change in resistance is plotted vs annealing temperature for Cu/Si and Cu/CoNiO/Si test structures. It is seen from the results that in case of Cu/Si structure sheet resistance start increasing after 100 °C whereas in case of Cu/CoNiO/Si structure sheet resistance remains almost constant up to 400 °C. These results show that CoNiO barrier was stable up to 400 °C.

XRD patterns of Cu/Si and Cu/CoNiO/Si structures corresponding to different annealing temperatures are shown in figure 6.20. As shown in figure, for structure without barrier, degradation of main copper peak was observed at 150 °C and a new peak corresponding to Cu$_3$Si also appeared in the spectrum. In structure with barrier, the spectrum was unchanged up to 400 °C. New peak corresponding to Cu$_3$Si appeared in the spectrum at 450 °C.

At higher temperatures top copper layer starts degrading and that can be imaged using SEM technique. Figure 6.21 shows the SEM images of Cu/CoNiO/Si structure annealed at different temperatures. Figure 6.21 (a) shows that the copper layer in Cu/CoNiO/Si structure was stable even after annealing at 400 °C. In the case of Cu/CoNiO/Si structure the degradation was observed after annealing at 450 °C as shown in figure 6.21 (b).
Figure 6.19 % Change in sheet resistance of Cu/Si and Cu/CoNiO/Si structures

Figure 6.20 XRD patterns of test structures (a) Cu/Si and (b) Cu/CoNiO/Si
Now XRD, four probe and SEM results can be merged. XRD and four probe results showed that barrier was stable up to 400 °C. Same can be observed in SEM images as no significant changes were observed in surface of Cu/CoNiO/Si structure up to 400 °C. The microstructures or hillocks were seen at 150 °C and 450 °C for the Cu/Si and Cu/CoNiO/Si structures respectively. Thus the barrier was stable up to 400 °C.
6.3 Conclusion

In this work, Co, NiO and CoNiO were characterized as diffusion barrier between Cu and Si to study the thermal stability. Both Co and NiO were found to be stable up to 350 °C whereas CoNiO was stable up to 400 °C in Cu/Barrier/Si stack.
References
