Chapter 3
Adsorption and Diffusion Studies of Ni/W System

Adsorption is a process where molecules or atoms from a gas phase bind in a condensed layer on a solid or a liquid surface [88]. It becomes important to distinguish between two radically different kinds of adsorption viz. chemisorption and physisorption. The first one occurs if there is a significant change in the electronic structure by the formation of direct bonds, whereas there is no direct bonding in physisorption and the adsorbate is held on the substrate by the Van der waals forces only. The main concern of the present work is to study the chemisorption of nickel on the tungsten single crystal planes. Isolated metal atoms are very reactive, as they possess unsaturated valence orbitals. They react easily with other metal atoms on a substrate having different electronegativities forming chemical bonds. The variations in the electronic charge structure modify the height of the electrostatic barrier leading to a change in the workfunction [89]. As the workfunction tends to follow the change in electronegativities, the magnitude and direction of its change can be used as a measure of electronic charge transfer between the substrate and the adsorbate. Inference regarding the adsorbate coverages can also be drawn from the change in the workfunction.

The atoms adsorbed on the surfaces can cause changes in the surface structure of the substrate. The adatoms occupy their preferred sites. Once almost all such sites are occupied (a situation generally termed as monolayer), the second layer starts forming with further incident adatoms. In all these processes, the structure of the surface is modified and thus, the workfunction of the material, which depends on the structure, changes. It is possible to investigate the electronic and structural properties of these bimetallic systems by means of accurate measurements of workfunction variations of the substrate metal with the adsorbate coverage.

There has been a continuous progress in the understanding of the surface modification, due to its importance in the area of bimetallic catalyst systems as discussed...
in the literature review in Chapter 1. It is pertinent at this point to mention that most of the work carried out using non-field emission techniques is on macroscopic crystals, which are comprised of stepped surfaces. Field emission microscopy having a capability of producing ultra clean surfaces due to very high temperature cleaning and degassing, with smooth single crystal planes has been used to study the submonolayer coverages of nickel on tungsten single planes for the present work.

3.2 Experimental Aspects

Adsorption studies were performed in all glass probe hole field emission microscope tubes designed and fabricated indigenously (Schematic is depicted in Fig. 2.4). Typically a tube consists of a sharp specimen tip attached on to a tungsten loop on a four-pin glass pinch. The screen assembly is made of a phosphor coated molybdenum foil with a hole (1 mm dia) at the center and having a Faraday cup collector on the other side. The adsorbate source was prepared on a loop attached to a two-pin glass pinch. The geometry is such that the adsorbate atoms have a line of sight with the specimen substrate tip. This tube was then mounted on an all-metal UHV system. Clean UHV conditions were achieved by liquid nitrogen cooled titanium sublimation pump backed by the sputter ion pump. The getter bulb immersed in liquid nitrogen bath was fired continuously before the experiments.

The clean vacuum conditions were ensured by observing the stability of the field emission current, after cleaning the tip by degassing several times and by observing field emission pattern. Current measurements were done using a Keithely 614 electrometer. This procedure was repeated for various selected planes. The adsorbate dose was controlled by manipulating the source heating current and duration.

An arbitrary dose was deposited onto a <110> oriented tungsten field emitter tip. The adsorbate was equilibrated by heating the tip at a certain temperature for a fixed duration of time, after a dose is deposited (580K for 60 secs). After each deposition the Fowler Nordheim (FN) characteristics were recorded. The tungsten planes chosen for the
observations were W(110), W(100), W(111), W(112). The method of magnetic deflection was used to bring the planes of interest onto the probe hole.

The workfunction $\varphi$ of the adsorbate-covered surface can be calculated from slopes of the ten-point Fowler Nordheim plots as

$$\varphi = \varphi_0 \left( \frac{m}{m_0} \right)^{2/3}$$

where, $\varphi_0$ is the average workfunction for the clean surface; $m$ and $m_0$ are the slopes of Fowler Nordheim plots for adsorbate covered and clean surfaces respectively[8]. The variation in the workfunction upon adsorption is given by

$$\Delta \varphi = \varphi - \varphi_0$$

The changes in the pre exponential term upon adsorption are calculated by using the following relation

$$\ln B = \ln \left( \frac{A_0}{A} \right)$$

where, $A_0$ and $A$ are the pre exponential terms for the clean and the adsorbate covered surfaces respectively. In case of the adsorption studies described in this chapter, $\Delta \varphi$ and $\ln B$ is plotted in terms of coverage. The maximum error in the calculation of workfunction was found to be 0.01 eV.

### 3.3 Results (Adsorption studies of nickel on tungsten)

The variations in the relative workfunction ($\Delta \varphi$) and in the corresponding pre-exponential factor ($\ln B$) with nickel coverage, have been obtained for total tip surface as well as for single crystal planes of tungsten, viz. W(110), W(121) W(111) and W(100). The results for average W, W(110), W(121), W(111) elsewhere [90, 91].

Adsorption studies of nickel have been extensively carried out by deposition on tungsten field emitter held at elevated temperatures to investigate the effect of substrate temperature on the workfunction variations. Such studies have been conducted for certain planes like W(100) using other techniques [62]. Kolaczkiewicz and Bauer [92]
Fig 3. 1: The variations in: (a) the average workfunction ($\Delta\varphi$), (b) the corresponding changes in the pre-exponential factor ($\ln B$) with the number of arbitrary doses ($\theta$) of nickel, and (c) ($\Delta\varphi - \theta$) curve computed by Klein's Formula (300K).
investigated the effect of substrate temperature on the workfunction changes in the submonolayer coverage of gold on tungsten. Substrate temperature was found to be responsible for a two-dimensional phase transition in this case.

Measurements have been done for total tip surface and other single crystal planes of W mainly W(110), W(121), W(111) and W(100) for four different substrate temperatures viz. 500K, 630K and 760K. The range of temperature has been carefully chosen so as to avoid desorption of adsorbate from the emitter. Nickel atoms are desorbed at temperatures above 1300K. The experiments have been performed under identical conditions as carried out with the emitter held at 300K.

3.3.1 Average Workfunction

Deposition at 300K

Fig. 3.1(a) shows average workfunction variation with nickel coverage in terms of number of doses. The workfunction measurements have been made from the slopes of the F-N plots. It has been observed that $\Delta \varphi$ increases and attains a constant value of about 0.52 eV. The increase in workfunction is accompanied by a decrease in In B as shown in Fig. 3.1(b).

![Fig 3.1](image1.png)

(a) Clean W tip (7.9kV) (b) Nickel adsorbed tip after 15 Doses (7.9 kV)

Fig 3.2: Field emission micrographs of (a) clean W tip (7.9kV) (b) nickel adsorbed tip after 15 Doses (7.9 kV)
Results on the variation of the average workfunction of nickel on tungsten, by Jones and Martin [59] are available for comparison. However, they have obtained the workfunction value by application of Klein's formula [93]. When the workfunction was calculated by using this formula, the results (see Fig. 3.1(c)) agree fairly well to those reported by them. Fig. 3.2 shows a typical sequence of field emission micrographs recorded for clean and at a stage of 15 doses adsorbed and equilibrated on the W emitter.

**Deposition at higher temperatures: 500 K, 630 K and 760 K**

Fig. 3.3(a) shows the variations in workfunction for the total tip surface with arbitrary doses of nickel at three different temperatures 500K, 630K and 760K. Workfunction is found to increase for all the three temperatures though the magnitudes of increase are different. At 500K and 630K, \( \Delta \varphi \) has reached a saturation value close to 0.1 eV whereas in the case of 760K it has reached up to 0.4eV. The corresponding changes in the pre-exponential term (\( \ln B \)) are shown in Fig 3.3(b).

**3.3.2 Ni/W(110)**

**Deposition at 300K**

Fig. 3.4(a) shows the \( \Delta \varphi - \theta \) curve for the W(110) plane. At 300 K, \( \Delta \varphi \) is found to decrease to a value -0.5 eV at 7 doses and thereafter it increases to a saturation value of 0.5 eV. Similar results have been observed for Ni/W(110) by Kolaczkiewicz and Bauer [60] and for Fe/W(110) by Adsool et al. [35]. Workfunction curve for 300K excellently matches with the data of Whitter and Gomer [67] who have also carried out workfunction measurements of nickel on W(110). The calculations for the Ni/W(110) by Rudnitsky [50] based on a simple theoretical model, matches well with the data obtained by us for this plane.

The corresponding changes in \( \ln B \) are shown in Fig. 3.4(b). The field emission micrograph shows a decrease in size of the W(110) plane (Fig. 3.2).
Fig 3.3: The variations in the (a) average workfunction ($\Delta \varphi$) and (b) the corresponding changes in the pre exponential factor ($\ln B$) with arbitrary nickel doses at 500K, 630K, and 760K.
Fig 3.4: The variations in the (a) workfunction ($\Delta \varphi$) and (b) the changes in the pre-exponential factor ($\ln B$) for W(110) with arbitrary nickel doses at 300K.
Deposition at higher temperatures: 5000 K, 630 K, 760 K

Fig. 3.5(a) shows the variation in $\Delta \phi$ for the W(110) with nickel coverage and the corresponding changes in the pre exponential factor is shown in Fig. 3.5(b) at 500K, 630K, 760K. The workfunction change ($\Delta \phi$) was found to increase to reach a value 0.5eV at 500K. However it was found to decrease for higher temperatures like 630K and 760K. The value of $\Delta \phi$ was saturated at -1.0eV at 630K and -1.2eV at 760K. The variation in ln $B$ for 630K and 760K is found to be substantial as compared to that observed for 500K.

3.3.3 Ni/W(121)

Deposition at 300K

Fig. 3.6(a) shows the $\Delta \phi$ - $\theta$ curve for the W(110) plane. In case of Ni/W(121), $\Delta \phi$ decreases in two steps to reach a saturation value -0.45 eV at 300 K (see Fig. 3.6(a)). These results are in good agreement to those of Kolaczkiewicz et al. [60]. Similar results on Co/W(121) have been observed by Sharma [36]. The corresponding changes in ln $B$ are shown in Fig. 3.6(b).

Deposition at higher temperature: 500 K, 630 K and 760 K

The variations in the workfunction $\Delta \phi$ and the corresponding changes in the pre exponential factor with nickel coverages on W(121) are shown in Figs 3.7(a, b). Workfunction was found to increase in case of all the three temperatures. However a sharp reversal of the trend was observed in the case of 500K after reaching a minimum of -1.2eV. At 630K, $\Delta \phi$ decreased in two steps to a value of 0.8eV at 16 doses, whereas at 760K, $\Delta \phi$ remained constant at -0.6eV upto coverage of 10 doses after an initial decrease. The value was found to saturate at -1.2eV.

3.3.4 Ni/W(111)

Deposition at 300K

Fig. 3.8(a) shows the usual $\Delta \phi$ - $\theta$ curve for the W(111) plane at 300 K. $\Delta \phi$ in this case increases initially to a value ~ 0.36 eV and then falls to ~ 0.2 eV. After 5 doses $\Delta \phi$
Fig 3.5: The variations in the (a) workfunction ($\Delta \varphi$) and (b) the changes in the pre-exponential factor ($\ln B$) for W(110) with arbitrary nickel doses at 500K, 630K and 700K.
Fig 3.6: The variations in the (a) workfunction ($\Delta \phi$) and (b) the changes in the pre-exponential factor ($\ln B$) for W(121) with arbitrary nickel doses at 300K.
Fig 3.7: The variations in the (a) workfunction ($\Delta \phi$) and (b) the changes in the pre-exponential factor ($\ln B$) for W(121) with arbitrary nickel doses at 500K, 630K and 700K.
Fig 3.8: The variations in the (a) workfunction ($\Delta\phi$) and (b) the changes in the pre-exponential factor ($\ln B$) for W(111) with arbitrary nickel doses at 300K
again increases to saturate at a value of ~ 0.48 eV. The corresponding changes in \( \ln B \) are shown in Fig. 3.8(b).

**Deposition at higher temperatures: 500 K, 630 K and 760 K**

Fig. 3.9(a) shows the variation in \( \Delta \phi \) for the W(111) with nickel coverage and the corresponding changes in the pre exponential factor is shown in Fig. 3.9(b). At 500K, \( \Delta \phi \) was found to increase monotonically to reach a saturation value at 0.4eV. The \( \Delta \phi \) was found to decrease and saturate at 0.62eV after and initial increase upto 5 doses, where the reversal in trend was observed. At 760K, \( \Delta \phi \) is found to decrease to reach a value of 0.6eV at coverage of 16 doses.

3.3.5 Ni/W(100)

**Deposition at 300K**

In the case on Ni/W(100), \( \Delta \phi \) is found to decrease in the first two doses and remained constant for the following six doses as shown in Fig. 3.10(a). Beyond 8 doses it again showed a decreasing trend till 17 doses. Fig. 3.10(b) shows a constant decrease in the pre-exponential factor.

**Deposition at higher temperatures: 500 K, 630 K and 760 K**

Fig. 3.11(a) shows the workfunction variations at higher temperatures viz, 500K, 630K and 760K and Fig. 3.11(b) shows the variations in the corresponding \( \ln B \). The variation in workfunction is found to depend on the substrate temperature. At 500K and 760K the work function started increasing only after 5 doses to reach a maximum value at 8 doses and further it was found to decrease. Workfunction was observed to decrease monotonically at a substrate temperature of 760K.

3.4 Discussion

The variations in the workfunction (\( \Delta \phi \)) and in the pre-exponential term (\( \ln B \)) with the nickel coverage (\( \theta \)) on various single crystal planes of tungsten can be explained in terms of the geometrical and electronic structure of the ad surfaces. Field emission
Fig 3.9: The variations in the (a) workfunction ($\Delta \phi$) and (b) the changes in the pre-exponential factor ($\ln B$) for W(111) with arbitrary nickel doses at 500K, 630K and 700K.
Fig 3.10: The variations in the (a) workfunction ($\Delta \varphi$) and (b) the changes in the pre-exponential factor ($\ln B$) for W(100) with arbitrary nickel doses at 300K.
Fig 3.11: The variations in the (a) workfunction ($\Delta \varphi$) and (b) the changes in the pre-exponential factor ($\ln B$) for W(100) with arbitrary nickel doses at 500K, 630K and 700K.
microscopy results based on workfunction variations alone are not sufficient enough to make conclusive remarks on the behaviour of nickel on tungsten surfaces. Hence, best efforts are taken to compare the results with the data obtained by others on similar systems, by field emission and other techniques. However, there are minor differences in the 'values' of workfunction obtained by others, though the trend of variations in the workfunction was found to be matching. These are expected due to the differences in the respective surface techniques used and their varied experimental conditions. This is also due to the fact that non-field emission techniques use macroscopic crystals, which consist of stepped surfaces.

(a) Electronic Structure Consideration

Nickel is a transition metal having 8 electrons in $3d$ shell. The electronic arrangement in this shell is close to its completely filled configuration ($d^{10}$). Compared to iron and cobalt nickel has a sharp band structure[70]. The electron affinities of nickel and tungsten are 1.156 eV and 0.815 eV respectively whereas the electronegativities of both the metals are nearly equal. Therefore, it may be proposed that when a nickel atom is brought near the substrate tungsten atom, it tends to acquire electrons from the substrate atom to attain a more stable configuration. This electronic charge transfer from substrate to adsorbate possibly causes an increase in the average workfunction of nickel covered tungsten surfaces. Various physical properties of nickel and tungsten are summarized in Table 3.1 for this purpose.

(b) Geometrical Considerations

The behaviour of the workfunction variations on single crystal planes is mostly governed by the geometrical aspects viz. the crystal structures on nickel and tungsten, atomic arrangement on each single crystal plane of the substrate and also the atomic sizes of nickel and tungsten.

Nickel exists in fcc phase at 300 K while tungsten is in bcc phase. Atomic sizes of tungsten and nickel are 1.37 Å and 1.24Å respectively. Because of different atomic sizes,
# Physical Properties

<table>
<thead>
<tr>
<th></th>
<th>Co</th>
<th>W</th>
<th>Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Crystal Structure</strong></td>
<td>fcc</td>
<td>bcc</td>
<td>fcc</td>
</tr>
<tr>
<td><strong>Atomic Radius</strong></td>
<td>1.25 Å</td>
<td>1.37 Å</td>
<td>1.24 Å</td>
</tr>
<tr>
<td><strong>Ionisation Energy</strong></td>
<td>7.86 V</td>
<td>7.98 eV</td>
<td>7.64 eV</td>
</tr>
<tr>
<td><strong>Electron affinity</strong></td>
<td>0.662 eV</td>
<td>0.815 eV</td>
<td>1.156 eV</td>
</tr>
<tr>
<td><strong>Electronegativity</strong></td>
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<td>1.7</td>
<td>1.8</td>
</tr>
<tr>
<td><strong>Electron Configuration</strong></td>
<td>3d(^7)4s(^2)</td>
<td>5d(^4)6s(^2)</td>
<td>3d(^8)4s(^2)</td>
</tr>
<tr>
<td><strong>Lattice Constant</strong></td>
<td>3.55 Å</td>
<td>3.16 Å</td>
<td>3.52 Å</td>
</tr>
<tr>
<td><strong>Average Workfunction</strong></td>
<td>4.41 eV</td>
<td>4.54 eV</td>
<td>5.10 eV</td>
</tr>
<tr>
<td><strong>Polarizability (in cc)</strong></td>
<td>(7.5 \times 10^{-24})</td>
<td>(11.1 \times 10^{-24})</td>
<td>(6.8 \times 10^{-24})</td>
</tr>
</tbody>
</table>

Table 31
nickel forms strained overlayers on the tungsten surfaces. This strain is mainly due to the lattice mismatch. The misfit parameters in case of W(110), W(121) and W(111) planes are calculated and listed in Table 3.2. The superposed planes of bcc substrate and fcc adsorbate are determined by the best geometrical fit at the adsurface. The atomic models for the substrate planes and the superposing adsorbate planes have been given in Figs. 3.12-15. The degree of strain in the nickel overlayers on various single crystal planes of tungsten have been calculated and given in the respective figures.

3.4.1 Average Workfunction

*Deposition at 300K*

As is evident from Figs. 3.1(a) and (b), the increase in the average workfunction suggests that nickel is adsorbed mainly as electronegative element on tungsten. The average workfunction increases and attains a constant value of about 0.52 eV at 10 doses. The increase is obtained from the total emission, which is the collective contribution from all substrate crystal planes. It may be noted that the emission from each plane is different and the total emission will reflect the contribution coming from the maximum emitting plane. Hence, the overall increase in the workfunction is attributed to the increase in the workfunction of W(110) and W(111) planes. The increase in the workfunction in our case is accompanied by a decrease in In B.

In Co/W system [36], decrease in the average workfunction is observed. As cobalt has 7 electrons in the 3d shell, its probable tendency is to loose two electrons and to attain a more stable half filled configuration. Thus the reduction in the workfunction of Co/W system is attributed to the electronic charge transfer from cobalt atoms to tungsten atoms.

*Deposition at higher temperatures: 500 K, 630 K and 760 K*

The average workfunction is found to increase for all three temperatures studied for the present work. At 500K and 630K, the workfunction has increased to saturate at a value of 0.1eV and 0.12eV respectively. The increase in the workfunction is however small in comparison to the value (0.52eV) at room temperature. This could be attributed
<table>
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<tr>
<th>Substrate</th>
<th>Adsorbate</th>
<th>Misfit (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tungsten (BCC)</td>
<td>Nickel (FCC)</td>
<td></td>
</tr>
<tr>
<td>(110)</td>
<td>(111)</td>
<td></td>
</tr>
<tr>
<td>$a = 3.16 \text{Å}$</td>
<td>$a = 2.49 \text{Å}$</td>
<td>+ 21.2 (stretching)</td>
</tr>
<tr>
<td>$b = 2.74 \text{Å}$</td>
<td>$b = 2.49 \text{Å}$</td>
<td>+ 9.5 (stretching)</td>
</tr>
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<td>$\theta = 60^\circ$</td>
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</tr>
<tr>
<td>$n_{\text{max}} = 1.22 \times 10^{19} \text{atoms/m}^2$</td>
<td>$n_{\text{max}} = 1.88 \times 10^{19} \text{atoms/m}^2$</td>
<td>- 52.45 (Reduction in atomic density)</td>
</tr>
<tr>
<td>(111)</td>
<td>(111)</td>
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<tr>
<td>$a = 4.47 \text{Å}$</td>
<td>$a = 2.49 \text{Å}$</td>
<td>+ 44.29 (stretching)</td>
</tr>
<tr>
<td>$b = 3.87 \text{Å}$</td>
<td>$b = 2.49 \text{Å}$</td>
<td>+ 35.65 (stretching)</td>
</tr>
<tr>
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<td></td>
</tr>
<tr>
<td>$n_{\text{max}} = 5.78 \times 10^{18} \text{atoms/m}^2$</td>
<td>$n_{\text{max}} = 1.86 \times 10^{19} \text{atoms/m}^2$</td>
<td>- 221.79 (Reduction in atomic density)</td>
</tr>
<tr>
<td>(121)</td>
<td>(110)</td>
<td></td>
</tr>
<tr>
<td>$a = 4.47 \text{Å}$</td>
<td>$a = 3.52 \text{Å}$</td>
<td>+ 21.2 (stretching)</td>
</tr>
<tr>
<td>$b = 2.74 \text{Å}$</td>
<td>$b = 2.49 \text{Å}$</td>
<td>+ 9.12 (stretching)</td>
</tr>
<tr>
<td>$\theta = 90^\circ$</td>
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</tr>
<tr>
<td>$n_{\text{max}} = 8.16 \times 10^{18} \text{atoms/m}^2$</td>
<td>$n_{\text{max}} = 1.14 \times 10^{19} \text{atoms/m}^2$</td>
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<tr>
<td>(100)</td>
<td>(110)</td>
<td></td>
</tr>
<tr>
<td>$a = 3.16 \text{Å}$</td>
<td>$a = 3.52 \text{Å}$</td>
<td>- 11.4 (compression)</td>
</tr>
<tr>
<td>$b = 3.16 \text{Å}$</td>
<td>$b = 2.49 \text{Å}$</td>
<td>+ 21.2 (stretching)</td>
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</tr>
<tr>
<td>$n_{\text{max}} = 1.0 \times 10^{19} \text{atoms/m}^2$</td>
<td>$n_{\text{max}} = 1.14 \times 10^{19} \text{atoms/m}^2$</td>
<td>- 14.0 (Reduction in atomic density)</td>
</tr>
</tbody>
</table>

Table 32 (Misfit Parameters)
to the roughening of the surface as compared to the adsorption on the surface at 300K. It has been proposed by Kolaczkiewicz and Bauer [40] that the adsorbate forms a two dimensional gas on the substrate surface at high temperatures, causing a large change in the surface roughness in the atomic level. This will give rise to a decrease in the workfunction. It is interesting to note that the workfunction is increased in the first few doses and then came back to 0.0eV at 630K and 760K. From this a steady and fast increase in the workfunction was observed. At 760K, the value has increased monotonically to reach a value close to 0.4eV. Although it is difficult to make any conclusive remarks about this behaviour on the total emitter surface, it can be attributed to the possibility of alloying effects on some of the individual crystal planes at this temperature. Alloying is reported to occur on W(121) and W(100) planes by the studies carried out by Kolaczkiewicz and Bauer [60] and Berlowitz and Goodman [94].

3.4.2 Ni/W(110)

*Deposition at 300K*

In case of W(110) plane, which is smooth and compact, the workfunction initially decreases linearly by ~ 0.5 eV to reach a minimum at 7 doses and then it increases to reach a saturation value of ~ 0.5 eV above 10 doses. The results are well matching with those obtained by Kolaczkiewicz and Bauer[60], Whitter and Gomer[67] on the W(110). Whitter and Gomer has attributed the initial decrease in the workfunction on this plane to the charge transfer from nickel to tungsten. The initial decrease in the workfunction is also due to the nickel induced surface states as suggested by C. Koziol et al [70]. It is felt however that the geometry plays important roll in controlling the workfunction at submonolayer coverages. Ni/W(110) system has been reported to be unusual because, though nickel adsorption upto one monolayer is pseudomorphic, the saturation coverages in the monolayer corresponds to 1.29 ML [67]. At very low temperatures, a layer by layer growth of nickel is observed on W(110) [67, 74]

Initial decrease in the workfunction of W(110) plane is also due to the increase in the emitting area around this plane, as seen in the field emission pattern. The degree of
Substrate W(110) Plane

\[ a = 3.16, \quad b = 2.74, \quad \theta = 109.47^\circ \]

Adsorbate Ni (111) Plane
(Obtained by calculating minimum misfit)

\[ a = 2.488, \quad b = 2.488, \quad \theta = 60^\circ \]

Misfit = 21.2% along \( a \)

= 9.5% along \( b \)

Fig. 3.12: Model of the atomic arrangement of the W(110) and Ni(111) plane
strain in the nickel adlayer on W(110) has been calculated by determining the best geometrical fit of the adsorbate and the substrate. In case of W(110) plane, Ni(111) plane seems to superpose to give rise the minimum strain. The degrees of strain in the pseudomorphic layer in two directions are found to be about 21.2% and 9.12%. This lattice mismatch causes the strain in the nickel overlayers on the W(110). Similar behaviour was observed by Kolaczkiewicz et al. [67] by using retarding field workfunction measurement technique. The workfunction minimum ($\Delta \phi = 0.76$ eV) was found to occur at the completion of first pseudomorphic layer. The workfunction was reported to increase as the coverage increases. This increase was attributed to alloying after completion of the first layer. In the present case, coverage equivalent to 7 doses corresponds to the completion of first pseudomorphic layer. The increase in the workfunction beyond one monolayer coverage may be attributed to surface alloying. The variation in $\ln B$ with number of doses (see Fig. 3.4(b)) shows a zero crossover at 7 doses. This is suggestive of surface reconstruction [95]. Reconstruction on the W(110) plane has also been suggested by Adsool et al. [35] for Fe/W system.

**Deposition at higher temperatures: 500 K, 630 K and 760 K**

The workfunction variations have been found to be strongly dependent on the temperature. At 500K, the $\Delta \phi$ is found to increase to a value of 0.5eV. This behaviour is opposite to that observed at 300K where an initial decrease of $\Delta \phi$ is followed by an increase suggesting a surface rearrangement. This can be supported by the field ion microscope observation of Jones and Martin [59] that a disordered pattern of nickel was observed when heated at 300K on a field evaporated tungsten tip and, there was a definite ordering when the annealing temperature was raised to 600K. At higher temperatures 630K and 760K, the $\Delta \phi$ is found to decrease monotonically to reach a saturation value of -1.0 eV and -1.25eV respectively. This could be due to the formation of islands with the island edges contributing prominently to the electron emission at low coverages [67]. Field ion microscopy results reported by Bassett [72] showed that nickel grows as chains on the W(110) surface in the $<111>$ direction at low coverages and these islands coalesce
into two dimensional islands at higher coverages. K. Besocke and H. Wagner [96] reported strong influence of the surface atomic arrangement on the workfunction variations upto a temperature of 700°C. The surface rearrangements of the substrate atoms are also expected. The possibility of surface alloying of nickel on W (110) upto 1 monolayer is less as reported in the literature earlier [67].

3.4. 3 Ni/W(121)

*Deposition at 300K*

As evident in Fig. 3.6(a), Δφ decreases slowly and attains a saturation value -0.5 eV at 300 K, at a coverage of about 10 doses. The corresponding changes in ln B indicate an increase in the emitting area. W(121) is a channeled plane and atomically smooth in one direction and rough in other directions with “troughs and crests”. At low coverages the atoms go into the “valleys”(crests) and produce a smoothening effect as explained by Kolaczkiewicz and Bauer [60] supported by their observations using low energy electron diffraction (LEED). Nickel atoms being smaller in size can well be accommodated in these sites. This smoothening effect causes an increase in the W(121) workfunction upon adsorption of nickel. The reduction in the workfunction of W(121) plane may also be due to the enhanced emission from the surrounding regions as seen from the field emission pattern. The degree of strain in Ni/W(121) layer is 21.2% along [110] direction and 9.12% along [111] direction.

*Deposition at higher temperatures : 500K, 630K and 760K*

The workfunction variations Δφ for all three temperatures 500K, 630K and 760K are found to decrease at low coverages. At 500K, Δφ - θ curve showed a minimum at 2 doses and then increases monotonically. W(121) is a plane having a smooth atomic arrangement in one direction and rough in the other direction. The reduction in the workfunction for 500K may be attributed to the surface roughening caused by the adsorption of nickel on the W(121). Kolaczkiewicz and Bauer [60] explained the reduction in the low coverage region as due to the expelled nickel atoms after
Substrate W(121) Plane

$\alpha = 4.47$, $b = 2.74$, $\theta = 90.0^\circ$

Adsorbate Ni (110) Plane
(Obtained by calculating minimum misfit)

$\alpha = 3.52$, $b = 2.49$, $\theta = 90^\circ$

Misfit = 21.2% along $a$
= 9.12 % along $b$

Fig. 3.13: Model of the atomic arrangement of the W(121) and Ni(110) plane
compression to the densely packed rows on the W(121) plane causing the atomic roughness to increase. Island formation may be expected since the mobility of the nickel atoms is comparatively less at this temperature. As the coverage increases this island may coalesce to make the surface smooth leading to an increase in the workfunction. At 630K and 760K there is a monotonous decrease in the workfunction. This could be due to the possibility of surface alloying by the formation of pseudomorphic double layer of Ni₄W on the W(121) even at very low coverages as reported by Kolaczkiewicz and Bauer [60].

3.4.4 Ni/W(111)

Deposition at 300K

As seen in Fig. 3.8(a), $\Delta \phi$ is found to increase and attains a saturation value of about 0.48 eV for the nickel adsorption on the W(111) plane. The W(111) having an open structure with an atomically rough surface, the increase in the workfunction may be due to the smoothening of this plane. Kolaczkiewicz and Bauer [64] studied growth and thermal stability of Ni/W(111) crystal face by $\Delta \phi$ measurements, LEED and AES. The results are in excellent agreement with those observed in the present study. The workfunction minima obtained by us on 5 arbitrary doses matches with the minima observed by Kolaczkiewicz et al. at 1 monolayer. The position and values of the minima are however dependent on the coverage and annealing conditions as reported by these authors. It is clear that, the coverage required to form monolayers on different planes varies depending on the structure and the experimental conditions viz. deposition rate, annealing etc. [64]. The values of the workfunction maxima can also differ due to the isolated nickel atoms present elsewhere on the plane having a larger dipole strength [67].

Similar increase in the workfunction of W(111) plane was observed for Fe/W system [35]. The strain in the pseudomorphic layer of nickel on W(111) is about $+44.29\%$ and $+35.65\%$ along [110] and [121] directions.
Substrate W(111) Plane

\[ a = 4.47, \ b = 3.87, \ \theta = 90^0 \]

Adsorbate Ni (111) Plane
(Obtained by calculating minimum misfit)

\[ a = 2.488, \ b = 2.488, \ \theta = 60^0 \]

Misfit = 44.29\% along \(a\),
= 35.65\% along \(b\)

Fig. 3.14: Model of the atomic arrangement of the W(111) and Ni(111) plane
Deposition at higher temperatures: 500 K, 630 K and 760 K

At 500K, the workfunction of the W(111) is found to increase monotonously to saturate at value close to 0.5eV. This observation is in consistent with that observed at 300K where the increase took place in two steps. W(111) has an open structure with a rough atomic arrangement. At low coverages and low temperatures nickel atoms are expected to produce a smoothing effect by accommodating in the open structure of the plane. Field ion microscope observations by Jones and Martin [59] revealed the nickel overlayers on the W(111) with high effective workfunction as qualitatively seen from the field emission micrograph of the same configuration.

The increase in the workfunction in the lower coverages was observed at 630K with a reversal in trend at around 5 doses. After that the workfunction showed a monotonous decrease to reach a saturation value at ~0.625 eV. This low coverage increase in the workfunction may also be attributed to the surface smoothing. However, at coverages greater than 5 doses, the workfunction decreases till saturation observed at 14 doses. At 760K also, there is a monotonous decrease in the workfunction. This may be explained as due to the surface alloying effects. Intermixing (only upto 10%) of nickel in the W(111) is reported by Chenzhi et al. [63]. These authors do not observe faceting of nickel on this plane. Report of nickel on W(111) by Kolaczkiewicz and Bauer [64] shows that nickel grows pseudomorphically on the W(111) at room temperature upto one monolayer. Further in the next 3 layers, there is a structural rearrangement and 3D crystallites start growing beyond 4 monolayers.

3.4.5 Ni/W(100)

Deposition at 300K

Workfunction decreases monotonously up to coverage of around 16 doses. This decrease in the effective workfunction can be explained with the geometrical strain produced in the Ni-W interface. At the very low coverages, formation of scattered nickel atoms on the smooth W(100) plane leads to a reduction in the effective workfunction.
Substrate W(100) Plane

\[ a = 3.16, \ b = 3.16, \ \theta = 90.0^\circ \]

Adsorbate Ni (110) Plane
(Obtained by calculating minimum misfit)

\[ a = 3.52, \ b = 2.49, \ \theta = 90^\circ \]

Misfit = -11.39% along \( a \)
= +21.26% along \( b \)

Fig. 3.15: Model of the atomic arrangement of the W(100) and Ni(110) plane
Geometry plays a decisive role in controlling the effective workfunction of the adsorbate covered surfaces. Tungsten has a \( bcc \) structure with a smooth and compact \( W(100) \) plane having a workfunction of 4.8eV. Nickel being \( fcc \), the deposited layer is strained due to the lattice mismatch on the \( bcc \) tungsten substrate. Photoemission and Ion Scattering results of Overbury et al [62] indicate that the electronic effects is dominated by the interfacial strain in deciding the change in the surface properties of \( W(100) \) upon nickel adsorption. Smith and Anderson [58] have discussed the orientational relations for preferred growth directions at length.

The strain in the pseudomorphic layer of nickel on the \( W(100) \) plane is about \(-11.4\) \% and \(+21.2\) \% along \( a \)- and \( b \)-directions.

*Deposition at higher temperatures* : \( 500 \, \text{K}, \, 630 \, \text{K and} \, 760 \, \text{K} \)

At temperatures 500K and 630K, workfunction is found to increase after 4-5 doses to give a local maximum at around 8 doses and decreases with further coverage. The decrease becomes more prominent and monotonous as the substrate temperature is increased. Overbury et al. [62] observed a random alloy formation in the submonolayer coverage on \( W(100) \) with the tungsten atoms protruding above nickel atoms. This mixing was not observed when the substrate was annealed below 500K. A rippled surface, with nickel atoms occupying sites closer to the substrate than the neighboring tungsten atoms, is produced by alloying nickel into the first layer of nickel[62]. Hence, the steady decrease in workfunction can be attributed to the formation of the surface alloy phase on the \( W(100) \) with a rough topography. Alloy formation has been reported to occur on the \( W \) \((121)\) plane [60, 97]. Earlier field ion microscopy results [74,75] show that nickel atoms become just mobile above 337K. At temperatures above 600K, substrate tungsten atoms rearrange to accommodate more adatoms in the substrate lattice [98]. The workfunction was found to monotonously decrease at a substrate temperature of 760K. Smith and Anderson [58] have reported nucleation of nickel on the tungsten field emitter in the range of temperatures between 426K-650K. They have also observed the formation of tiny clusters at higher temperatures 600K-700K.
3.5 Temperature dependent growth of Nickel

Nickel doses have been deposited onto a tungsten field emitter at 300K and equilibrated (annealed) at two different temperatures. The growth pattern was found to be strongly dependent on the annealing temperature. Nickel doses equilibrated at 760K resulted in a “well spread” pattern. The sequence of field emission pattern is given in Fig. 3.16. A pseudomorphic pattern was seen in the field emission micrograph with only (110) and the (100) planes being dark. There was no preferential growth observed at this temperature. Figs. 3.17(a, b) show the corresponding variations in the workfunctions and $\ln B$ with coverage respectively. It can be seen that $A\phi$ is increased and reached a maximum of 0.6 eV at a coverage of 20 doses and decreased further to 0.4 eV and finally went to 0.5 eV for higher coverages. The total field emission current, however, decreased from 480nA to 90nA at constant voltage 7.9kV applied to the emitter. The pre-exponential term remains almost unaffected with coverage.

Figs. 3.18(a, b) show the variations in the workfunctions and $\ln B$ with coverage respectively, in the case of the annealing at 960K. The average workfunction increases initially with the number of doses and then starts decreasing from the 25 doses onwards. This decrease is due to the overgrowth of nickel observed on the W(111) plane of tungsten as seen in the sequence of field emission micrographs (Fig. 3.19). This overgrowth enhances the field factor locally and resulted in the large decrease in the effective workfunction. The recent results obtained by Kolaczkiewicz and Bauer [64] showed that the variations in the workfunction and the growth pattern depend on the annealing conditions. Faceting of Ni on W(111) was observed by these authors on the W(111) plane. Lattice misfit is known to cause faceting [64], which is maximum in the case of W(111) with Ni(111) face. The nickel growth is the Stranski-Krastanov mode as described by Kolaczkiewicz et al. [64]. The enhancement in the field factor is also suggested by a large change in the pre-exponential factor. Thus the observed change in the workfunction is only apparent. The formation of Ni-W surface alloy is also a possibility at this temperature.
Fig. 3.16. Sequence of field emission micrographs for the nickel dose deposited at 300K and equilibrated at 760K.
Fig 3.17: The variations in the average (a) workfunction ($\Delta \varphi$) and (b) the changes in the pre-exponential factor ($\ln B$) for arbitrary nickel doses deposited at 300K and equilibrated at 760K.
Fig 3.18: The variations in the average (a) workfunction (Δφ) and (b) the changes in the pre-exponential factor (ln B) with arbitrary nickel doses deposited at 300K and equilibrated at 960K.
Fig. 3.19: Sequence of field emission micrographs for the nickel dose deposited at 300K and equilibrated at 960K.
It can be concluded from these observations that growth of nickel on the single crystal W surfaces is strongly dependent on the annealing temperature.

3.6 The $\Delta\phi$ measurements for W(121) and the W(100)

Workfunction variation measurements have been extended for (121) and (100) planes of tungsten for 960K anneal by using probe-hole field emission technique. The doses have been deposited at 300 K and equilibrated at 960K. The sequence of field emission patterns corresponding to the growth is same as Fig. 3.19 (tip-2 state).

3.6.1 Ni/W(121)

Fig. 3. 20(a, b) shows the variations in $\Delta\phi$ and In $B$ with the nickel coverage on the W(121) surface. The workfunction has been found to decrease in the first few doses corresponding to the submonolayer region. It reached a minimum at 10 doses (with $\Delta\phi = -0.75eV$). This is discussed in the earlier section and is attributed to the roughening of the W(121) plane. The work function is found to increase beyond 10 doses. One more minimum was observed at around 28 doses. A monotonous increase in the workfunction is observed beyond 42 doses with a zero cross over after 50 doses. The surface structure of this plane is peculiar because it has channels in one direction and hence, the plane can be treated as smooth in one direction and rough in the other. The reversal of change in $\Delta\phi$ is an indication of a restructuring on the W(121) plane.

3.6.2 Ni/W (100)

Fig. 3. 21 (a, b) shows the variations in $\Delta\phi$ and In $B$ with the nickel coverage for W(100) surface. A monotonous decrease in $\Delta\phi$ is observed till 20 doses to reach a minimum value $-1.75eV$. This decrease in workfunction is attributed to the scattered nickel atoms on the smooth W(100) surface at low coverage. Further, increase in coverage leads to occupation of the nearest neighboring sites and two-dimensional cluster formation [75] on the W(100). Beyond this, it may be seen as islands grow on this plane.
Workfunction Variation Ni/W(121) at 300 K

(a)

Multilayer Coverage

\[ \Delta \phi \]

Number of Dose

Pre-exponential factor Ni/W(121)

(b)

\[ \ln B \]

Number of doses

Fig 3.20: The variations in the (a) workfunction ($\Delta \phi$) and (b) the changes in the pre-exponential factor ($\ln B$) for W(121) with arbitrary nickel doses at deposited at 300K and equilibrated at 960K.
Fig 3.21: The variations in the (a) workfunction ($\Delta \phi$) and (b) the changes in the preexponential factor ($\ln B$) for W(100) with arbitrary nickel doses at deposited at 300K and equilibrated at 960K.
making the surface loose, resulting in the reduction of the effective workfunction. This is in good agreement with the results obtained by Berlowitz and Goodman [94] and Overbury et al. [12] for Ni on W(100). A very large variation in the corresponding Fowler Nordheim pre exponential factor clearly indicates that there is a large change in emitting area caused by structural rearrangements in this smooth plane. Hence, it can be concluded that the magnitude of the reduction in workfunction (-1.75eV) is only apparent and this is mainly attributed to the surface roughening effects by random distribution of adatom islands in the low coverage region. These islands may coalesce then to form a uniform layer on the substrate causing an increase in the effective workfunction after 60 doses. This inference matches well with the conjecture of Berlowitz and Goodman [94] that nickel grows layer by layer after the first monolayer. Nickel atoms were found to occupy the *four fold hollows* of the W(100) plane [62]

**Field Ion Microscopy Studies:**

Field ion microscopy system was completely modified with low temperature facility and better pumping systems during the thesis work as explained in Chapter 2. However, detailed work could not be done using field ion microscope due to some technical problems. The preliminary results using this field ion microscope have been obtained on the nucleation and growth of Ni/W system and are discussed in Appendix A.

### 3.7 Comparison with Fe/W and Co/W systems

It is worth comparing nickel adsorption with the adsorption data [35,36] on other 3d transition elements studied previously in this laboratory. A comparison has been made for the changes observed in the average workfunction of Fe and Co covered W surfaces. Fe/W is found to have shown a trend similar to that observed for the Ni/W system. The average workfunction in both the cases increases with the coverage. In case of Fe/W, the increase in the workfunction of the rough (111) and the (161) planes is more prominent and contributes mainly to the net increase in the average workfunction. Similarly, the
increase in the average workfunction of Ni/W system is due to the increase in the 
workfunction of (110) and (111) planes. However, studies on Co/W system show a 
reduction in the average workfunction. This is attributed to the significant reduction 
in the workfunction of high workfunction planes viz. (110) and (100). Hence, it can be 
understood that, iron and nickel are adsorbed on tungsten as electronegative elements 
while cobalt as an electropositive element. Nickel and cobalt was found to be strongly 
dependent on the substrate temperature in contrast to the behavior of iron.

3.8 Diffusion of nickel on W(100)

The nucleation of 3d transition metals, depends on the diffusion and mobility of 
atoms on the underlying surfaces. Hence, surface diffusion is one of the important surface 
phenomena of great interest. Diffusion in general is governed by thermodynamic 
considerations like chemical potential, the vapour pressure, concentration gradient etc. 
Atoms or a cluster of atoms can move in different directions to settle down at places to 
make the surface “smooth” or in more general terms, to reduce the surface energy. A 
close analogy of surface tension can be pointed out. Diffusion in solids can occur mainly 
by three different means; the first one being solid diffusion, where the atoms diffuse 
through the vacancies or equivalently the diffusion of vacancies in the opposite direction. 
Diffusion of atoms on a solid surface is another possibility where a thin layer of atoms is 
transported along the surface. Diffusion can also occur by evaporation, diffusion through 
the gas and condensation.

Field emission microscopy has been extensively used [20] for the studies of 
surface diffusion of adsorbed material on the tip surfaces. This is because of its ability to 
sense the arrival of atoms at a certain location as seen by the probe-hole. The 
measurements are usually made in terms of the workfunction variations. Single atom 
diffusion by field ion microscope experiments yield highly accurate measurements of the 
diffusion lengths and thus the diffusion coefficients of adatoms on various substrates.

Extensive work pertaining to diffusion processes occurring on various crystal 
surfaces of tungsten has been reported by many researchers using field emission
techniques. Field electron and ion microscopy (FEM/FIM) studies of the diffusion behaviour of single atoms of nickel on some planes of tungsten have been carried out by Flahive and Graham [73], Bassett [72] and Kellog [74,75]. Jones and Martin [59] and Blaszczyszyn and Blaszczychynowa [99] studied diffusion of nickel atoms on thermally cleaned W field emitters. Nickel deposited tungsten surfaces are known to possess good emission properties, which can find applications in various vacuum microelectronic devices [81-83].

3.8.1 Activation energy

Nickel atoms were deposited onto the tungsten tip and the voltage required for constant emission from W(100) has been monitored with annealing at a range of temperatures from 350K to 400K. The melting point of tungsten is much higher than that of nickel. At this temperature range, a surface rearrangement of tungsten is completely ruled out. Further, the solubility of nickel in bulk tungsten is very low [59, 60] and there is no intermixing of nickel reported in this temperature range. Hence it is expected that the only process that is taking place is diffusion of nickel atoms on the tungsten surface. The activation energy for diffusion has been estimated to be 0.78eV from the resulting Arrhenius plot (Fig. 3.22). This value is smaller compared to the value (1.01eV) obtained by Kellogg [75] from the single atom diffusion experiments. This is attributed to the fact that, the diffusion process observed by probe-hole field emission microscopy is the gross effect of many nickel atoms on the probed (100) region. Thus it is expected to be different from the single atom movements on the plane where nickel adatom-adatom interaction does not come into picture. There is no field emission data available on the diffusion of Nickel on the W(100) surface under similar conditions for a comparison. However, the experiments carried out for the present study are closer to the diffusion experiments carried out by Jones & Martin [59] using field emission microscopy where nickel atoms deposited, are allowed to spread over the entire emitting area of the entire tip surface. The diffusion process in this has been explained by the “unrolling carpet mechanism”.
Fig. 3.22: Arrhenius plot for diffusion of nickel on W(100) surface in the temperature range 350K - 400K. Time (t) has been the estimated duration for the voltage to rise from 90% to 100% of the saturation value for a particular temperature (T).
Several attempts for measuring the activation energies for nickel on the W(110) and W(111) have been made. However, saturation could never be reached with a fixed dose at certain temperature when many times the experiments were repeated.

3.9 Conclusions

Adsorption and growth of nickel on tungsten single crystal planes have been studied for room temperature and three higher temperatures (500K, 630K, 760K). A pseudomorphic growth of nickel was observed in the submonolayer coverage with an increase in the average workfunction. Workfunction variations on individual planes of tungsten with nickel coverage indicated the dependence of geometry of the interface on the workfunction change. Following conclusions are drawn from adsorption studies of nickel on various single crystal tungsten surfaces:

1. At 300K, workfunction decreased for smooth planes like W(110), W(121) and W(100). This is, in general, due to the surface roughening of these smooth planes. It was found that the workfunction of W(111) increased due to smoothening.

2. Workfunction measurements at higher temperatures indicated strong dependence on temperature. The average workfunction was found to increase in all the three temperatures studied. At 630K and 760K the average workfunction decreased for all the single crystal planes studied viz. W(110), W(121), W(111) and W(100). The behaviour at 500K was found to be different. It is expected that the change in this behaviour is due to the substrate surface rearrangement and surface alloying at higher temperatures.

3. Growth studies of nickel also showed a strong dependence on the annealing temperature. Annealing at 960K resulted in “two spot” pattern whereas 760K annealing lead to a “well spread” pattern. An apparent reduction in the
workfunction was observed in case of 960 K anneal due to the enhanced field factor. However, the workfunction was found to increase with coverage upon annealing at 760K. Probe-hole field emission microscopy studies on the growth of nickel on the W(121) and W(100) surface indicated a reduction in the workfunction in the low coverage region followed by an increase in both the cases.

4. Diffusion of nickel on W(100) has been studied for low temperature range (350-400K). The activation energy for diffusion has been calculated to be 0.78eV.