

THIN FILM DEPOSITION, FORMATION OF NANOPARTICLES & VARIATION OF RESISTANCE OF DEPOSITED SAMPLE WITH TEMPERATURE

G SUDHEER KUMAR¹ & JAGIRDAR V RAMANA RAO²

¹Defence Institute of Advanced Technology, Pune, Maharashtra, India

²Jawaharlal Nehru Technological University, Hyderabad, Andhra Pradesh, India

ABSTRACT

The ability to deposit thin films of various materials is important for the fabrication of modern microelectronic devices and for enabling a variety of investigations of fundamental physical principles. There are many techniques for controllably depositing thin films onto a substrate with thicknesses as small as a few nm. And Nanoparticles are commonly defined as particles less than 100 nm in diameter. Due to this small size, nanoparticles have a high surface-to-volume ratio. This increases the surface energy compared to the bulk material. The high surface-to-volume ratio and size effects (quantum effects) give nanoparticles different chemical, electronic, optical, magnetic and mechanical properties from those of the bulk material. In this paper, we used thermal evaporation technique to deposit Nickel layer on silicon wafer & the deposited sample post annealed at different temperatures in vacuum and or different gas environments, and the sheet resistance of the films was measured using conventional four/two probe method.

KEYWORDS: Ni Deposited Thin Film, Thermal Evaporation Technique, Annealing, Nanoparticles, Sheet Resistance, Temperature

INTRODUCTION

The emerging field of nanotechnology is leading to exceptional understanding and control over the fundamental building blocks of all materials. At the core of nanotechnology is the ability to work at or near the atomic level in order to create large structures with fundamentally new and advantageous structural organizations. Nanostructured materials include atomic clusters, layered (lamellae) films, filamentary structures, and bulk nanostructured materials. The common thread to these materials is the nanoscale dimensionality, i.e. at least one dimension less than 100 nm, more typically less than 50nm. In some cases, the physics of such nanoscale materials can be very different from the macroscale properties of the same substance, offering often superior properties that warrant much interest in these materials.

The ability to deposit thin films of various materials is important for the fabrication of modern microelectronic devices and for enabling a variety of investigations of fundamental physical principles. There are many techniques for controllably depositing thin films onto a substrate with thicknesses as small as a few nm. In this paper, we will focus on one deposition technique- thermal evaporation- and produce thin metal film.

Many of the new, highly advantageous behaviors of nanoparticles, and of bulk materials made of nanoparticles, are not easily predicted from those observed at macro scales. The most important changes in behavior are caused not simply by size reduction, but by new properties intrinsic to or becoming predominant at the nanoscale. These phenomena include quantum confinement or size quantization and predominance of interfacial phenomena. Understand the basic control of processing parameters, chemistry, and nucleation processes of nanoparticles should allow generation of tailor-made nanoparticles of tightly controlled chemistry for a wide range of applications.

The temperature dependence follows an exponential relation with temperature, $R=R_0e^{-\alpha/t}$. $\alpha=E_{\text{gap}}/2k_b$ where E_{gap} is the bandaged and k_b is the Boltzmann constant.

BACKGROUND

Requirements for Filaments: Electrically Conductive, High melting point, Good thermal shock resistance, Filament should be wettable by the charge materials, Low solubility for the Charge materials.

Table 1: Evaporation Temperatures

Material	Evaporation Temperature, °C	Comments
Zinc	325	High vapor pressure at RT
Aluminum	1390	
Copper	1516	
Chromium	1612	
Lead	1680	Toxic
Iron	1829	
Nickel	1848	

All materials evaporate, even at room temperatures. Heat simply accelerates the process.

Equilibrium Vapor Pressure. Cadmium... Rhenium.

In nanotechnology, a particle is defined as a small object that behaves as a whole unit in terms of its transport and properties. Particles are further classified according to size: in terms of diameter, coarse particles cover a range between 10,000 and 2,500 nanometers. Fine particles are sized between 2,500 and 100 nanometers. Ultrafine particles or nanoparticles are sized between 100 and 1 nanometers. The reason for this double name of the same object is that, during the 1970-80's, when the first thorough fundamental studies were running with "nanoparticles" in the USA (by Granqvist and Buhrman) and Japan, (within an ERATO Project) they were called "ultrafine particles" (UFP). However, during the 1990s before the National Nanotechnology Initiative was launched in the USA, the new name, "nanoparticle" had become fashionable. Nanoparticles may or may not exhibit size-related properties that differ significantly from those observed in fine particles or bulk materials. Although the size of most molecules would fit into the above outline, individual molecules are usually not referred to as nanoparticles. Nanoclusters have at least one dimension between 1 and 10 nanometers and a narrow size distribution. Nanopowders are agglomerates of ultrafine particles, nanoparticles, or nanoclusters. Nanometer-sized single crystals, or single domain ultrafine particles, are often referred to as nanocrystals. Nanoparticle research is currently an area of intense scientific interest due to a wide variety of potential applications in biomedical, optical and electronic fields.

According to the band theory, the energy levels of semiconductors can be grouped into two bands, the valence band and the conduction band. In the presence of an external electric field it is the electrons in the valence band that can move freely, thereby responsible for the electrical conductivity of the semiconductors. In case of intrinsic semiconductors the Fermi level lies in between the conduction band minimum and valence band maximum. Since the conduction band lies above the Fermi level, at 0K, when no thermal excitations are available, the conduction band remains unoccupied. So conduction is not possible at 0K, and resistance is infinite. As temperature increases, occupancy of the conduction band goes up, thereby resulting in decreases of electrical resistance of the semiconductor. The temperature dependence follows an exponential relation with temperature, $R=R_0e^{-\alpha/t}$. $\alpha=E_{\text{gap}}/2k_b$ where E_{gap} is the bandaged and k_b is the Boltzmann constant.

History

- i. End of 19th century - unusual properties of deposits on the walls of glass discharge tubes eroded interest of researchers: optical & electrical properties (P. Drude, Ann. der Physik, 36(1889)532).
- ii. 1927: electron diffraction on thin films (Davison - Germer)
- iii. 1930th - practical application: high reflectivity surface mirrors with non- conducting substrates
- iv. 1940th- vacuum and thin film (PVD) techniques, devices;
 - Electron microscopy (Ruska);
- v. 1960th- in situ electron microscopy (Bassett, Pashley, Poppa, Pócza, Honjo);
 - Surface decoration (Bassett, Bethge, Distler);
 - Ultrahigh vacuum technique;
 - Surface analytical methods:
 - Auger spectroscopy, LEED, SEM, ESCA;
 - Structure zone model:
 - Compilation of experimental results (Movchan-Demchishin)
- vi. 1970th - high resolution (also surface imaging) and analytical TEM (Halle School);
 - Chemical vapor deposition (CVD);
 - Computer simulation:
 - Atom-by-atom structure building (Gilmer&Bennema, Barna, Thomas et al; Dirks&Leamy)
 - Molecular beam epitaxy (MBE);
 - CERMET (nanocomposite) resistor films (Neugebauer);
- vii. 1980th - atomic resolution surface imaging techniques:
 - STM, AFM (Binning&Röhrer)
 - Atomic layer epitaxy;
 - Electron energy loss analysis - dedicated scanning TEM;
- viii. 1990th - aberration corrected ultrahigh resolution analytical TEM (Urban);
- ix. 2000th - advent of in situ techniques (UHV TEM, fast STM, synchrotron)

THIN FILMS HAVE TAKEN A PROMINENT PART IN

- Revolutionary development of new active and passive elements, devices and industries.
- Metamorphosis of society to "information society.

Although nanoparticles are generally considered an invention of modern science, they actually have a very long history. Nanoparticles were used by artisans as far back as the 9th century in Mesopotamia for generating a glittering effect

on the surface of the pots. Even these days, pottery from the middle Ages and Renaissance often retain a distinct gold or copper colored metallic glitter. This so called luster is caused by a metallic film that was applied to the transparent surface of a glazing. The luster can still be visible if the film has resisted atmospheric oxidation and other weathering. The luster originated within the film itself, which contained silver and copper nanoparticles dispersed homogeneously in the glassy matrix of the ceramic glaze. These nanoparticles were created by the artisans by adding copper and silver salts and oxides together with vinegar, ochre and clay, on the surface of previously-glazed pottery.

The object was then placed into a kiln and heated to about 600 °C in a reducing atmosphere. In the heat the glaze would soften, causing the copper and silver ions to migrate into the outer layers of the glaze. They're the reducing atmosphere reduced the ions back to metals, which then came together forming the nanoparticles that give the color and optical effects. Luster technique showed that ancient craftsmen had a rather sophisticated empirical knowledge of materials. The technique originated in the Islamic world. As Muslims were not allowed to use gold in artistic representations, they had to find a way to create a similar effect without using real gold.

The solution they found was using luster. Michael Faraday provided the first description, in scientific terms, of the optical properties of nanometer-scale metals in his classic 1857 paper. In a subsequent paper, the author (Turner) points out that: "It is well known that when thin leaves of gold or silver are mounted upon glass and heated to a temperature which is well below a red heat (~500 °C), a remarkable change of properties takes place, whereby the continuity of the metallic film is destroyed. The result is that white light is now freely transmitted, reflection is correspondingly diminished, while the electrical resistivity is enormously increased."

Vacuum Thermal Evaporation

The vacuum thermal evaporation deposition technique consists in heating until evaporation of the material to be deposited. The material vapor finally condenses to form of thin film on the cold substrate surface and on the vacuum chamber walls. Usually low pressures are used, about 10^{-6} or 10^{-5} Torr, to avoid a reaction between the vapor and atmosphere.

At these low pressures, the mean free path of vapor atoms is the same order as the vacuum chamber dimensions, so these particles travel in straight lines from the evaporation source towards the substrate. This originates 'shadowing' phenomena with 3D objects, especially in those regions not directly accessible from the evaporation source (crucible). Besides, in thermal evaporation techniques the average energy of vapor atoms reaching the substrate surface is generally low (order of kT , i.e. tenths of eV).

This affects seriously the morphology of the films, often resulting in a porous and little adherent material. In thermal evaporation techniques, different methods can be applied to heat the material. The equipments available in the laboratory use either resistance heating (Joule effect) or bombardment with a high energy electron beam, usually several KeV, from an electron beam gun (electron beam heating).

Electron Beam Heating Evaporation

This technique is based in the heat produced by high energy electron beam bombardment on the material to be deposited. The electron beam is generated by an electron gun, which uses the thermionic emission of electrons produced by an incandescent filament (cathode). Emitted electrons are accelerated towards an anode by a high difference of potential (kilovolts). The crucible itself or a near perforated disc can act as the anode. A magnetic field is often applied to bend the electron trajectory, allowing the electron gun to be positioned below the evaporation line (see diagram)

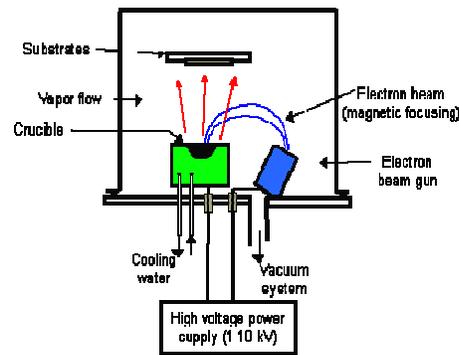


Figure 1: Electron Beam Heating Evaporation

As electrons can be focalized, it is possible to obtain a very localized heating on the material to evaporate, with a high density of evaporation power (several kW). This allows to control the evaporation rate, from low to very high values, and best of all, the chance of depositing materials with high melting point (W, Ta, C, etc.). Cooling the crucible avoids contamination problems from heating and degasification. The following figure shows a diagram of the electron beam gun evaporation equipment available at our laboratory.

Thermal Evaporation in Vacuum

In the evaporation deposition technique, the material is heated until fusion by means of an electrical current passing through a filament or metal plate where the material is deposited (Joule effect). The evaporated material is then condensed on the substrate. Other ways of heating are used, such as an RF coil surrounding a graphite or BN crucible, where the material to be evaporated is fused. The assembly of the technique is simple and results appropriate for depositing metals and some compounds with low fusion temperature (Al, Ag, Au, SiO₂, etc.). Typical metals used as heating resistance are Tantalus (Ta), Molibdene (Mo) and wolfram (W), with vapor pressure practically zero at the evaporation temperature ($T_{\text{evap}} = 1000\text{-}2000\text{ }^{\circ}\text{C}$). When a helicoidal filament surrounds the material it is convenient that the evaporated material wets the metal. A scheme of the deposition equipment used in the laboratory is shown in the figure.

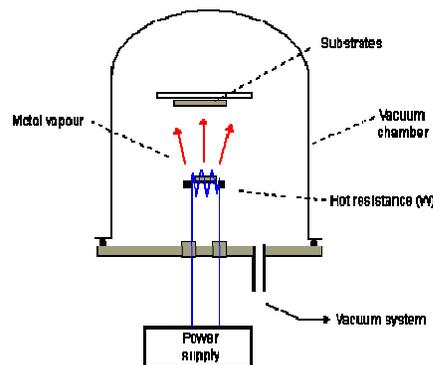


Figure 2: Thermal Evaporation in Vacuum

Four Probe Method

In this experiment, the four probe method of measuring resistance was used. The sample was mounted in an assembly, with four spring loaded contacts pressing the surface of the sample. The whole assembly was inserted into an oven. One of the main reasons of using a four probe method is that it practically eliminates the error due to contact

resistance. A constant current was passed through the two outer probes and the voltage across the two inner probes was measured using a digital voltmeter.

EXPERIMENTAL

Thin Film Deposition

Table 2: 100A⁰ Thin Layer of Ni Metal Deposited on Si Substrate by Evaporation Technique

Material to be Deposited: NICKEL
Substrate: SILICON
Vacuum: 2×10^{-4} mbarr
Deposited thickness: 100A ⁰
Deposition rate: 1.8A ⁰ /Sec at 1.19Amps to 5A ⁰ /Sec at 25Amps

Table 3: 200A⁰ Thin Layer of Ni Metal Deposited on Si Substrate by Evaporation Technique

Material to be Deposited: NICKEL
Substrate: SILICON
Vacuum: 3×10^{-4} mbarr
Depositing/deposited thickness: 200A ⁰
Deposition rate: 0.3A ⁰ /Sec at 1.22Amps to 5A ⁰ /Sec at 25Amps

Annealing

Annealing is a crucial step where prepared Ni layer is cracked into nanometric Ni-islands. In the present, Ni layer was heated up to several temperatures between 400°C and 800°C and kept during 15 min. NH₃ gas was used at 2 mbar and 20 sccm to keep a reducing atmosphere and avoid Ni oxidation.

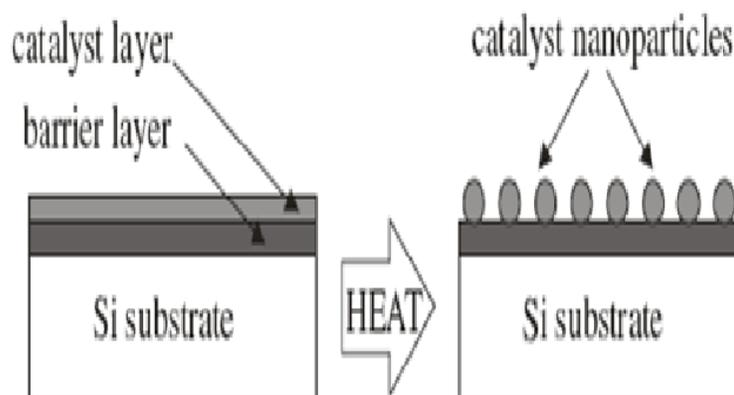


Figure 3: Effect of Annealing Process on Catalyst Layer

Electrical Resistance Measurement

Table 4: Surface Resistance vs Annealing Temperature of a Sample (100A⁰ Ni Deposited Silicon Substrate)

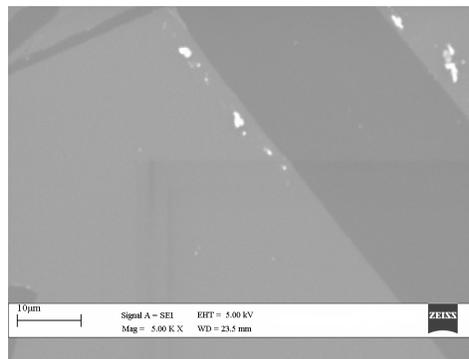
Annealing Temperature (°c)	Sheet Resistance of a Sample (Ω/sq)
400 ⁰ c	22.4MΩ
500 ⁰ c	51MΩ
600 ⁰ c	0.2GΩ
700 ⁰ c	0.5GΩ

Table 5: Surface Resistance vs Annealing Temperature of a Sample (200A⁰ Ni Deposited Silicon Substrate)

Annealing Temperature (°c)	Sheet Resistance of a Sample (Ω/sq)
400 ⁰ c	1.6 MΩ
500 ⁰ c	1.8 MΩ
600 ⁰ c	26 MΩ
700 ⁰ c	50 MΩ

RESULTS AND DISCUSSIONS

Fig 4. Is the SEM image of pristine sample which is taken after deposition of 100A⁰ thin layer of Ni metal on Si substrate by evaporation technique. In this figure we can clearly see the deposition of thin layers.

**Figure 4 : SEM Image of Pristine Sample**

100A⁰ Nickel film has been deposited on Silicon substrate (Fig 4) and annealed at different temperatures (Table 4) and observed the change on resistance increasing with increasing temperature (Fig 5) due to effect of breaking of thin film in nano islands on the silicon substrate. And the same sample is also characterized with Scanning Electron Microscopy, result image shown in Fig 7. There is the signature of isolation on nano islands on the Si substrate at the annealed temperature 700⁰C.

In this case (from Fig 5), at 400⁰c, the resistance is 22.4Mohms and at 500⁰c, the resistance is 51Mohms. So as the temperature increases, the resistance of the sheet also increases i.e., as temperature increases, the conductivity decreases due to the breaking of the thin film.

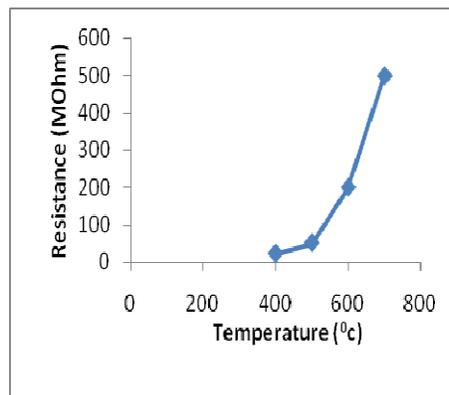


Figure 5: The Graph Shows the Resistance and Annealing Temperature Characteristics of a 100A⁰ Ni Deposited Si Sample

Similarly 200\AA Nickel film has been deposited on Silicon substrate and annealed at different temperatures (Table 5) and observed the change on resistance increasing with increasing temperature (Fig 6) due to effect of breaking of thin film in nano islands on the silicon substrate.

From Fig 6, at 400°C the resistance is 1.6Mohm and at 500°C , the resistance is 1.8Mohm . So as temperature increases, the resistance increases and conductivity of the material or sheet decreases. So we can say that at low temperature, the conductivity of the sheet or material is good or more.

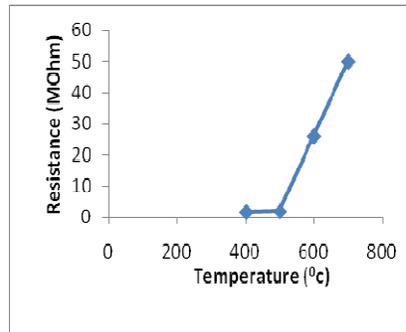


Figure 6: The Graph Shows the Resistance and Annealing Temperature Characteristics of a 200\AA Ni Deposited Si Sample

Fig 7 is the SEM image of Ni layer after Annealing at 700°C and found the formation of nanoparticles due to effect of mismatch of surface energy and different forces between the film and substrate. SEM image also shows the diameter of the particle.

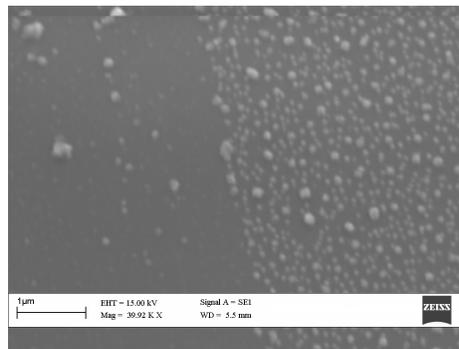


Figure 7: SEM Image of Ni Layer after Annealing at 700°C (This Image Shows the Formation of Nano Particles Whose Diameters are Less than 60nm)

CONCLUSIONS

A thin layer of Nickel metal was deposited on silicon substrate to develop basic understanding of thin film formation by thermal evaporation technique. A different thickness (10 and 20 nm) of Ni thin film has annealed at different temperatures $400, 500, 600$ and 700°C in vacuum and or different gas environments at 10^{-6} mbar base pressure to prevent the oxidization during the annealing. It was observed that the increasing the annealing temperature resulted in separation of Nano Island and increasing systematically, it also conforms with electrical resistance measurements of pristine and annealed samples at different temperatures. Parhat Ahmet et al. Also discussed the annealing effect of thin film on silicon substrate and observed the up to 300°C , they did not find any change of resistance. And Fig 7 also shows the formation of Nano Particles whose diameters are less than 60nm .

REFERENCES

1. Galasso, F.S., "Oxford, New York, Toronto, Sydney, Branschweig, Pergamon Press", **90** (1970).
2. Elfallal, I., Rilkington, R. D., Hill, A. E., *Journal of Thin Solid Films*, **223**, 303 (1993).
3. Ederth, J., Doctoral Degree Dissertation, Uppsala University, 4 (2003).
4. Nadaud, N., Lequeux, N., Nanot, M., Jove, J., Roisnel, T., *Journal of Solid State Chem.*, **135**, 140 (1998).
5. Devi, P. S., Chatterjee, M., Ganguli, D., *Materials Letters*, **55**, 205 (2002).
6. Nguyen, T.P., Le Rendu, P., Dinh, N.N., Fourmigue, M., Meziere, C., Young, G. O., *Synthetic Metals*, **138**, 229 (2003).
7. Luff, B.J., Wilkinson, J.S., Perrone, G., *Appl. Optics*, **36**, 7066 (1997).
8. Herrero, J., Guillen, C., *Vacuum*, **67**, 611 (2002).
9. Teixeira, V., Cui, H. N., Meng, L. J., Fortunato, E., Martins, R., *Journal of Thin Solid Films*, **420-421**, 70 (2002).
10. Balasubramanian, N., Subrahmanyam, A., *Journal of Material Science and Engineering*, **B1**, 279 (1988).
11. Hu, Y., Diao, X., Wang, C., Hao, W., Wang, T., *Journal of Vacuum*, **75**, 183 (2004).
12. Daoudi, K., Canut, B., Blanchin, M.G., Sandu, C.S., Teodorescu, V.S., Roger, J.A., *Materials Science and Engineering C* **21**, 313 (2002).
13. [Mirzae, F., Maleki, M. H., Mirjalili, G., 14th Conference on Optics and Photonics Proceedings, (2008).
14. M. Fleischmann, S. Pons. And M. Hawkins, *J Electroanal. Chem.* 261, 301 and errata in Vo1. 263, (1998).
15. H. Yuki, J. Kasagi, A. G. Lipson, T. Noda, T. Ohtsuki, B. F. Lyakhov, N. Asami: "Anomalous enhancement of DD-reaction rate in Au/Pd/PdO heterostructure targets under low energy deuteron bombardement", *JETP Lett*, **68**(11), 785, (1998).
16. D. C. Reynolds, D. C Look, B. Jogai and H. Morkoc *Solid State Commun.* 101, 9 (1997).
17. J. Lee, W. Choi, C. Kim, J. Hong, T.-U. Nahm and H. Cheong, *J. Korean Phys. Soc.* 49, 1126 (2006)

