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Modification of Electrical Properties of Metallic Thin Film By Plasma Irradiation

(Electrical Properties Modification By Plasma)

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***Abstract*— This work presents the modification of electrical properties of a Fe thin film by low pressure plasma irradiation technique. Using plasma surface modification technique we have modified the electrical properties of an iron-tungsten thin film. The materials are subjected to plasma for different time intervals under a particular plasma condition. The electrical properties like resistivity and capacitance are measured before and after exposure to plasma. Comparative studies show that the resistivity and capacitance of the thin film gets modifies substantially. The effect of temperature is also observed on the resistivity and capacitance of the thin film before and after exposure to plasma. The importance of this work lies in the modification of these properties due to plasma, which can be utilized in electronic device development and applications of thin film in different industrial and laboratory purposes.**

Keywords—Thin Film; surface modification; plasma treatment; electrical properties;

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I. INTRODUCTION

The electrical properties of various materials are determined by the presence of free electrons in materials. Because of the overlapping of the valence band and the conduction band in conductors it allows easy transmission of electrons, which is responsible for its high electrical conductivity. The flow of the electrons is opposed when a potential difference is applied across a conductor because of its internal property. This property of a conductor and in general for materials is termed as the resistivity. The resistance of conducting materials is not dependant on its shape and size. Resistance offered can be termed as the level to which a conducting material opposes the flow of current through it. Because of this resistance the energy gets converted from electrical energy into heat, light, or other forms of energy. Henceforth, there may be loss of electrons from the outer shell of the metallic atoms and they acquire an ionic state under the influence of a potential difference. The Coulomb collision between the ions and the electrons causes the resistance. In room temperature the ions has kinetic motion because of its thermal energy and due to which the electrons are scattered. This is the primary reason for resistance. Various factors like temperature, pressure, presence of impurities in a conductor and imperfection of lattice also affects the resistance.

This work deals with the modification of electrical properties of a thin film after irradiation by plasma. It is found that the electrical properties of bulk and a thin film are different. The difference between the properties of thin films and bulk materials is considered to be caused by the structure defect, boundary scattering (surface scattering, and grain boundary scattering). Because of the large variation in the dimension in its width in thin films, the scaling factor also plays a role in deciding the electrical properties of thin film materials by the same way. The film thickness, the lattice dimensions, the purity, the surface roughness, and the imperfect level of the layer plays a significant role in defining the type, mechanism, and stability of the electrical transport. It is now well known that if the thin film has thickness of the order of nano scale, then it’s all electrical, magnetic and optical properties changes. All electrical, magnetic and optical properties are defined by electron structure of materials. According to quantum electrical theory, electrical conduction in metals is due to electrons, while electrical resistivity results from the scattering of these electrons by the lattice [1, 2]. Because of the reduced size of the thickness electron scattering not only takes place inside the material but also is enhanced in the vicinity of surfaces. In case of bulk materials the free electrons are mostly confined at distances from the surface, because of their mean free path from the surface. Since for thin films the surface to volume ratio is much higher than it is for the bulk, surface scattering is a major factor affecting the film’s resistivity.

Because of the intensive applications of thin films in electronic industries for manufacturing of components and devices or for making of sensors, behavior of electrical properties of thin films under different context gained lot of interest amongst the material scientists. The extensive use of plasma for surface modifications has been widely reported in the literatures. The surface properties like in case of biomaterials [3] are modified, which changes the functional groups and enhances its properties. Textile fibers [4, 5] properties are also highly enhanced by plasma surface treatment. In our previous works on PEEK polymers [6, 7] and by other workers on polymers [8] it was demonstrated that by doing surface modification of the polymers its adhesive properties can be greatly improved. Not only for non metallic substances plasma is also used to modify the surface properties of metallic surfaces like Cu_3N, which is used as optical storage devices [9]. It has been observed that plasma irradiation of surfaces greatly modifies their surface properties. Akihiro Ikeda, et. al [10] has showed that the electrical characteristic properties of thin silicon oxynitride films gets substantially enhanced in regard to positive charge trapping, interface state density, leakage current, and stress immunity under an optimal nitrogen plasma exposure time of nearly 30 s. The results obtained by them are very interesting considering the use of such thin films in gate insulators for electrically-erasable non-volatile memory (Flash memory).

The study of thin semiconducting films is also very important because of its huge scale application in the electronic industries. One of the major parameter of study of such films has been on its temperature effect. It is seen that the electrical properties of thin films of Te deposited by evaporation technique shows a noticeable change at different temperatures [11]. From the analysis of mobility variance w.r.t. temperature it is shown that the grain boundaries are mainly responsible for the scattering of the holes. Moreover, it can also be verified that from the temperature dependence of the carrier concentration the films are doped with various acceptors, which follows a uniform distribution pattern in the forbidden energy gap.

The electrical properties are not only modified in metallic thin films but also get modified in superconducting thin strips [12]. The importance of thin film is of great interest. But when the size of such films approaches to nano scale it properties gets modified. It is observed that the electrical conductivity, resistance–temperature coefficient, and in-plane thermal conductivity of the nanofilms are much smaller than the corresponding bulk values from 77 to 330 K. [13 - 16]. Thin films of $La_{0.6}Sr_{0.4}FeO_{3-\delta}$ of different thicknesses exhibit different conductivity values at different temperatures. The electrical conductivity of the films increases with increasing film thickness but it is less when compared to that of the bulk material. The apparent conductivity versus temperature shows a maximum at a certain temperature and then varies [17].

Yang-Ming Lu, et. al. experimented the effect of hydrogen plasma treatment on Cu_2O film doped with nitrogen. They have observed that the dangling bonds of Cu may be terminated resulting in increase of the carrier concentration, which leads to decrease in the resistivity of the films [18]. Hydrogen plasma treatment can also reduce the surface roughness and increase the average grain size of hydrogenated nanocrystalline silicon (nc-Si:H) films [19]. Low power density plasma treatment for short duration (10 s) can significantly enhance the crystalline volume fraction and electrical conductivity, compared to as-deposited film. The possible reason for such change in its electrical behavior was attributed to the mass transport of Si atoms on the surface by surface and grain boundary diffusion. Because of the ferromagnetic property of iron it is often employed along with the antiferromagnetic chromium in Fe/Cr multilayers, which exhibit giant magnetoresistance effects. In Ref. [20] the authors in their work with FeF 3 crystallized thin films observed that the electrical conductivity of such films in temperatures ranging from 77-500 K changes, which is because of an electronic transfer between localized states in the gap. New thin film materials and methods for growth and modification of their properties are therefore actively pursued. In our present work, we will present the effect of low pressure air plasma produced by d.c. glow discharge method on electrical conductivity of thin film of Fe-W.

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II. EXPERIMENTAL METHOD

A. *Description of the experimental setups.*

We have used thermal evaporation technique to do a physical vapor deposition of a thin layer of iron in a glass substrate. The deposition takes place layer by layer on the glass surface producing a layered structure. The thermal vapor deposition system consists of a cylindrical vessel connected to a rotary pump and backed by diffusion pump. The inside view of the system is shown in Fig.1. We can produce a vacuum of the order of 10^{-6} mbar. Inside the chamber metallic plates are there, which are connected to a variable high d.c. current source. Tungsten filaments are connected between these plates for thermal heating of the materials for deposition. A piezo sensor is also present, which gives the thickness of deposition. Another steel plate is placed above the filament at a distance of 25 cm approximately from the filament. There is a square cut out in the plate which is just above the filament. The substrate on which deposition is to be made is placed at this hole. The thermal vapors from the filament are directly deposited on the substrate.

For plasma surface modification we have produced plasma in a cylindrical stainless steel vessel of 37 cm long and 21 cm inner diameter as shown in the schematic diagram in Fig 2. The vessel was evacuated to a base pressure of 10^{-4} mbar using a rotary pump. Then air was inserted in a controlled manner and a constant working pressure of 0.2 mbar was maintained. Air plasma was produced by discharging the gas between two circular steel plates of 5 cm diameter each and at a separation of 15 cm between them. The plates were coated on the outer surfaces by some non conducting coating materials to avoid discharge between the plates and the vessel body. The anode was electrically grounded. D.C. voltage was applied between the plates using a variable dc power supply of 1 KV and 1A. Discharge current was measured using a milliammeter (1 mA – 25 mA). A resistance in series with the milliammeter was used as a safety measure.

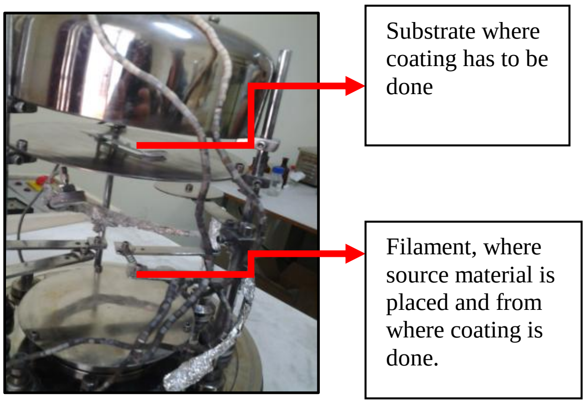

Fig. 1. The inside of the thermal evaporation system with the different parts where substrate and source material is placed.

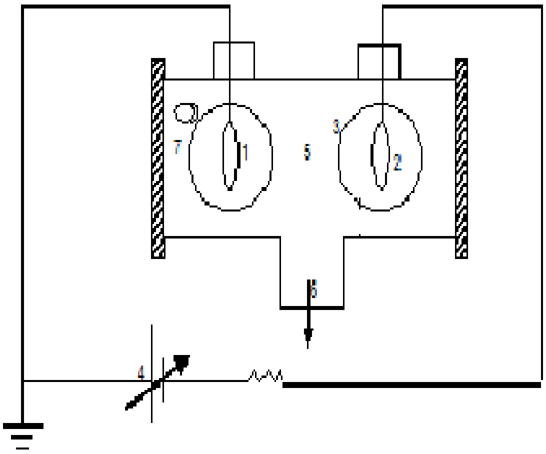

Fig. 2. Schematic diagram of the experimental setup. 1.anode, 2.cathode, 3.view-port, 4.DC supply, 5.vacuum chamber, 6.connection to rotary pump, 7.air inlet.

B. *Experimental procedure for thin film deposition*

The coating is done with thermal vapor evaporation technique by passing high current through the filament. The surface coating is done at a very low pressure to avoid contamination during evaporation due to oxidation or presence of other gases and evaporated particles can travel directly to the deposition target without colliding with the background gas. The system is a cylindrical vessel which is evacuated to a very low pressure. Initially the chamber is connected to rotary pump and evacuated to a pressure of 10^{-3} mbar. Then it is switch to bracking and made the pressure to go down to 10^{-4}-10^{-5} mbar. After that the diffusion pump is used to further lower the pressure of the order of 10^{-6} m bar. Once the pressure chamber attains a steady state condition the filament is slowly heated by varying the current through the filament so that the metallic strip in the filaments inside the chamber starts melting. After 10-30s, the metal starts melting and gets deposited on the glass slide.

For producing the deposition we have used standard size of samples of iron (Fe) of 95% purity. Number of thin rods of iron of length 53.80 mm and diameter of 1.10 mm were cut from a long wire of iron of the same diameter. They are then flattened into thin strips by mechanical hammering so that it will be easier to melt. These thin samples were cleaned with sand papers and acetone. This thin metallic strip was taken for ultrasonic bath in liquid base made with mixture of diluted sulphuric acid, phosphoric acid and with little amount of diluted nitric acid. It was cleaned for thirty minutes with heating. The thin strip was taken out from the ultrasonic bath and dried. After that the surface coating chamber was cleaned with acetone using surgical gloves, cotton and some cloth to remove the precipitations from previous depositions. Four metallic strips of weight of 1.8 grams were kept in a filament inside the surface coating chamber. Here thin metallic strip act as the source material for deposition on the glass slide. On the glass slide capillary tubes separated by equal distance were attached with the help of teflon on the substrate for creation of thin strips on the glass slide and coating on the capillary tubes. The glass slide was placed above the filament at a certain distance where coating has to be done.

The current is then further increased so that it gets evaporated and gets deposited on the glass slide placed on the top. Since the current through filament is high enough a part of the tungsten also gets evaporated along with iron. The deposition has a percentage of tungsten along with iron. After 30 s and visualizing the vanishing of the strips from the filament, the gate valve is closed and diffusion pump is shutdown. Then rotary pump is shutdown and the chamber is slowly brought down to the atmospheric pressure slowly. Uniform strips of thin layer of Fe with some impurities of tungsten are produced. The tungsten impurities are added during the heating of the source material.

C. *Experimental procedure for plasma irradiation*

The discharge chamber was first cleaned with acetone and was connected to the power supply. The chamber is associated with a rotary pump evacuated in a similar manner as explained for the thermal vapor deposition system. For producing glow discharge plasma with air we did not produce a very low pressure. We only use a rotary pump to evacuate to a pressure of 10^{-3} mbar. Before evacuating the sample was placed inside the vessel. After evacuating to a pressure of 10^{-3} mbar we insert air to bring the working pressure to 0.2 mbar. After that the dc voltage is applied between the two electrodes in the chamber for producing the plasma. We start measuring plasma current at approximately 320 V but the voltage is increased to get plasma current of 10.59±0.5mA so that the plasma density and power is high. Collisional plasma is produced and distinct glow from the plasma is observed. The samples were treated with plasma for different time intervals for which the same plasma condition is maintained for a specific time. The samples that were treated are then tested for their electrical and magnetic properties. Different fresh samples of thin films are used for each of the different exposure times.

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D. *Measurement of electrical properties*

The glass slide where the thin layer is deposited is taken to measure its electrical properties. The electrical properties like resistance, capacitance and inductance using LCR-Q meter were measured. Firstly, the resistance and capacitance reading of that thin film were noted at the room temperature. Similar measurements are carried out for samples with different plasma irradiation time under the same plasma generation conditions.

Each time the electrical properties are measured than the effect of heating is also carried out. The thin film was heated using a heating plate device to some degree of temperature which was measured by a thermometer. After some high temperature at about 75°C was reached, heating was stopped. The readings of resistance and capacitance of the thin film with the temperature were noted till the room temperature is reached.

Similar types of thin films were taken for the plasma treatment in the glow discharge chamber. Samples were prepared and different samples were used for different exposure times like 1, 2, 3………10 minutes individually. After every time interval it was taken to measure its resistance and capacitance and noted down their values. Next the sample was kept for about 1-2 hour and again its resistance and capacitance were measured. After the measurements taken at room temperature, the samples are heated to about 80-90°C. As the temperature was decreasing, the resistance and capacitance along with temperature value were measured. Measurements were taken till we get the room temperature. The sample was left for 24 hours. After 24 hours the electrical properties were again measured. Again we follow the same steps like heating and noted its properties at different temperature. The steps followed in the process are:

1. Heat the thin film till some temperature of about 80-90°C.
2. Take the readings of resistance and capacitance with increasing temperature.
3. Note down the readings of resistance and capacitance three times.
4. After temperature reaches 80-90°C, stop heating.
5. Take the readings of resistance and capacitance with decreasing temperature.
6. Note down the measurements till the room temperature is achieved.

III. RESULTS AND DISCUSSIONS

The experimental observations are discussed in this section The thin films produced are of few hundreds of nanometer. The first set of observations was taken for thin films before exposing to plasma. The resistance and capacitance of the film as measured before exposing to plasma at room temperature were 219 Ω and 152 μF. After that the same sample was heated and resistance and capacitance were measured at different temperature. The data observed for this varying temperature is plotted in Fig. 3.

From the plot it is evident that the resistance almost varies linearly with temperature till around 60^o C and then starts saturating as the temperature is increased. The resistance varies from 228.7 Ω at 30^o C to 243.9 Ω at 75^o C. As the temperature increases, surface scattering of the electrons perhaps also increases because of which the resistance increases. This nature is completely opposite to the resistance behavior of a bulk material with respect to temperature. Similarly the capacitance decreases with temperature and starts saturating toward higher temperature as shown in Fig. 4. The capacitance varies from a maximum of 151 μF to 146 μF in the same temperature range. Since the resistance increases with temperature the capacitance should decrease and is seen from the graph.

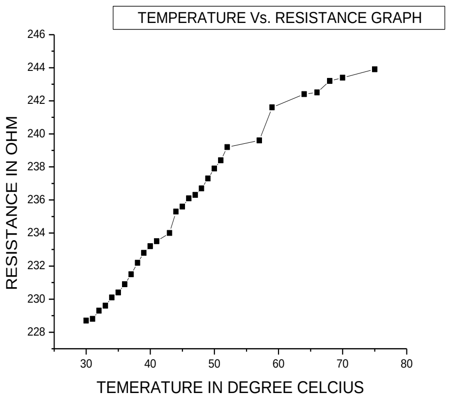

Fig. 3. Variation of the resistance of the unexposed thin film at different temperatures.

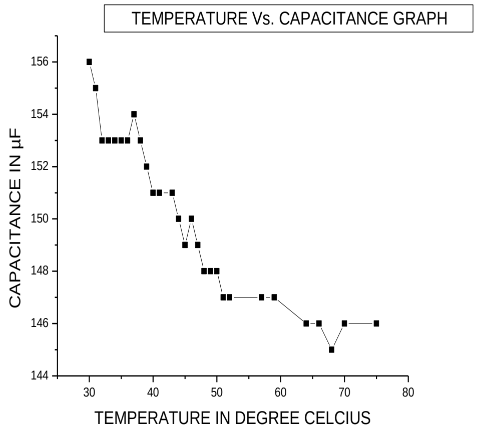

Fig. 4. Variation of the capacitance of the unexposed thin film at different temperatures.

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In Fig. 5, the variation of resistance of the thin film for different exposure time in plasma is shown. It is very interesting to observe that the thin film becomes more resistive with increasing the exposure time under the same plasma condition. The plausible reason may be adsorption of electrons at the surface because of which surface scattering of electrons increases further. A more detailed quantum mechanical investigation is necessary to understand this phenomenon. It was observed that the resistance varies from a minimum of 265.5 Ω for 60 s exposure time to 350.8 Ω for 600 s time. Likewise the variation of the capacitance is shown in Fig 6.

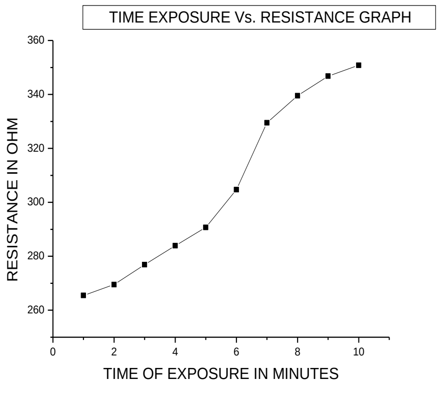

Fig. 5. Variation of the resistance of the thin film for different plasma *exposure time.*

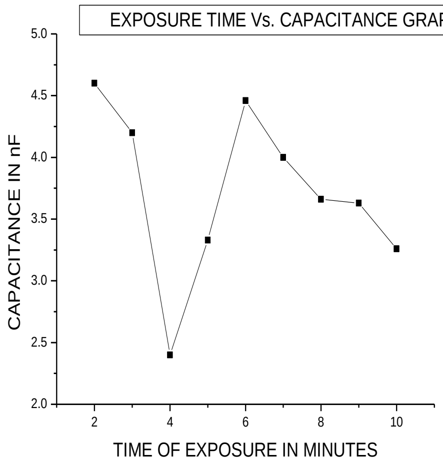

Fig. 6. Variation of the capacitance of the thin film for different plasma exposure time.

Except for an exposure time of 4 mins and 5 mins the capacitance decreases with increase of exposure time. The capacitance varies from 4.6 nF at 2 min exposure time to 3.26 nF for 10 mins exposure time. After that the samples were exposed to plasma for 1 hr and its resistance and capacitance were measured. Both values increases and they are approximately 402.6 Ω and 2.5 nF respectively. The samples are heated and the temperature variation of the resistance and capacitance are observed. The observations of the variations of resistance and capacitance with temperature exposed for 1 hr are given in Fig. 7 and 8.

The behavior of the resistance is still similar except that it initially decreases and then starts increasing with temperature and starts saturating around the same temperature of 65^{o} C. Hence we can say that the resistivity increases with increasing plasma exposure time and with heating. The difference is that with heating the resistivity starts saturating after some temperature. It is interesting to observe that the temperature from where saturation starts is independent of plasma exposure. The capacitance does not follow the expected behavior as seen in Fig 8. The pattern remains same for different samples under the same condition.

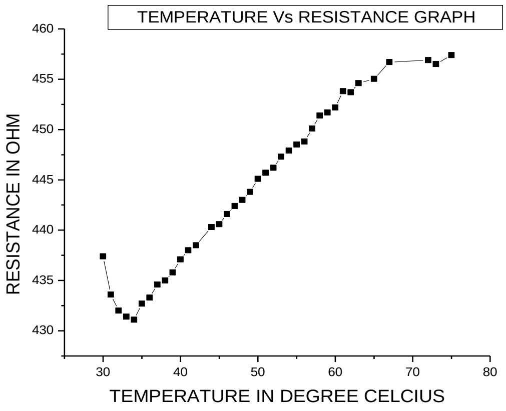

Fig. 7. Variation of the resistance of the thin film exposed under plasma for 1 hr.

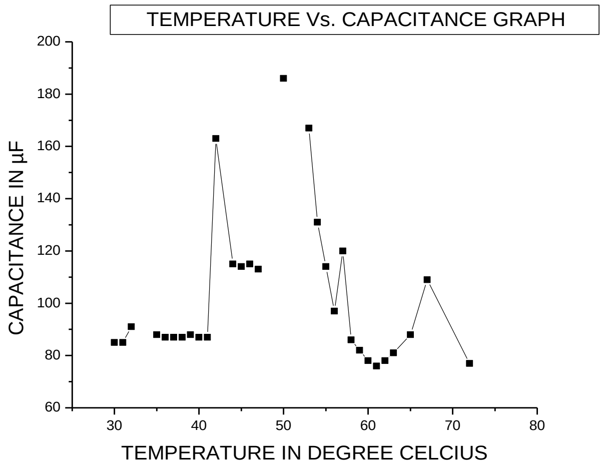

Fig. 8. Variation of the capacitance of the thin film exposed under plasma for 1 hr.

The probable reason may be that miniature thermal cracks might have developed with exposure time which affects the capacitance. In the last set of the experiments the samples were left over a day i.e. 24 hrs in desiccators. We carry out the same resistance and capacitance measurement process to see the atmospheric effect on the thin film. Basically the thin films should develop oxides due to the presence of moisture and oxygen, even though they were kept inside desiccators.

There was a marked change in the resistivity as was expected. The resistivity measured was in the range of kilo ohms and capacitance was in nano farad range. It varied from 1.08 KΩ at 30^{o} C to 1.168 KΩ at 90^{o} C. The capacitance varied from 0.19 nF to 2.9 nF for the same temperature range. The variation of the resistance and capacitance w.r.t. temperature is shown in Fig. 9 and 10. One of the reasons for substantial change in their values may be because of oxide formation. But the actual reason for this change requires a more theoretical and experimental observations about their change in their morphology. Quantum mechanical approach as mentioned in [1] will help us to understand such phenomena at a nanoscale.

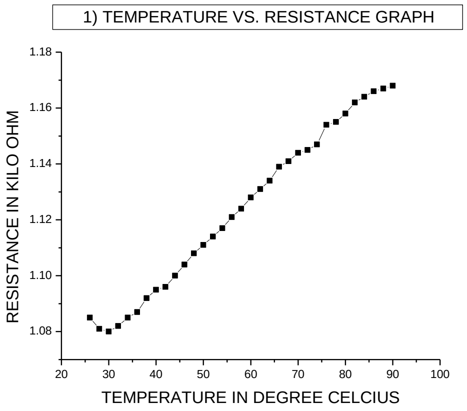

Fig. 9. Variation of the resistance of the thin film with temperature exposed under plasma after a gap of 24 hr.

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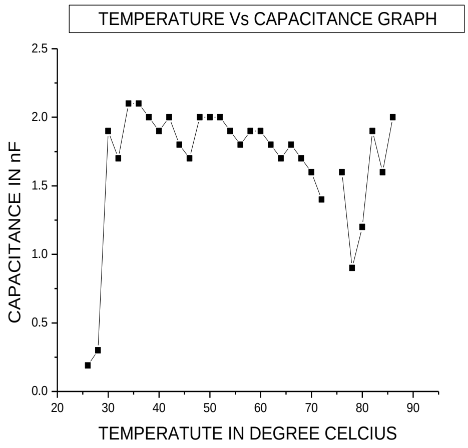

Fig. 10. Variation of the capacitance of the thin film with temperature exposed under plasma after a gap of 24 hr.

Overall the experimental results confirm that the electrical properties of Fe thin film with some tungsten impurities are greatly altered when exposed to a low pressure plasma as well as temperature variation. From the graphs obtained above we observed that the resistance of a thin film has increased as time of exposure increases but the capacitance decreases. The thin film characteristics are very well justified from our observations that the resistance should increase with temperature. In the whole experiment the effect of oxide formations during measurement of the electrical properties in air contact may have some effect, which was not included in our measurements.

IV. CONCLUSIONS

We see that the electrical properties of a thin film are greatly influenced by the plasma. Due to the plasma, the resistance has increased and it shows some new characteristic near the room temperature that instead of decreasing its resistance at decreasing temperature it starts increasing. This unusual behavior of temperature- resistance relationship is may be due to plasma effect. So, we found that the resistance of the thin film goes on increasing as exposure time and temperature increases, which may be attributed to scattering of surface phenomena. The capacitance variation behavior could not be established very accurately with plasma and temperature. This may be due to very low capacitance value and some affect of oxide formations. But the resistance has shown some good results. Such knowledge about the electrical conductivity behavior of Fe thin films under varying plasma condition is very useful for industrial purposes. More information can be derived by doing a morphological study to understand such characteristics.

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REFERENCES

[1] Tai Chang Chiang, “Quantum physics of thin metal films”, AAPPS Bulletin April 2008, Vol. 18, No. 2.

[2] U.S. Department of Energy Report on “Nanoscale science, engineering and technology research directions,” available at http://www.sc.doe.gov/bes/reports/files/NSET_rpt.pdf.

[3] H. Yamamoto, Y. Shibata, and T. Miyazaki, “Anode glow discharge plasma treatment of titanium plates facilitates adsorption of extracellular matrix proteins to the plates”, J Dent Res 84(7):668-671, 2005

[4] D. Sun et. al, “Investigating the plasma modification of natural fiber fabrics–The effect on fabric surface and mechanical properties”, Textile Res. J. 75(9), 639–644 (2005).

[5] A. Sparavigna, “Plasma treatments for textiles: an innovative technology for traditional and technical fabrics”, In Recent Res. Develop. Applied Physics, 5, (2002) 203.

[6] S. Jha et. al. “Experimental investigation into the effect of adhesion properties of high performance polymer modified by atmospheric pressure plasma and low pressure plasma: A comparative Study” J Appl Polym Sci. 118 (2010) 173.

[7] H. M. S. Iqbal et. al, “Comparative studies of adhesion properties of high performance polymer modified by atmospheric pressure plasma and low pressure plasma”, published in E. Schindel-Bidinelli (Ed.) Proceedings of Swiss Bonding 2009, pp (1-8). Bulachi (25th SWISSBONDING International Congress,) May 11-13, 2009 at Rapperswill, Switzerland.

[8] J.G.A. Terlingen, “Introduction of functional groups at polymer surfaces by glow discharge techniques”, University of Twente: Enschede, The Netherlands, 1993.

[9] A. Hojabri1, N. Haghighian1, K. Yasserian1, M. Ghoranneviss, “The effect of nitrogen plasma on copper thin film deposited by DC magnetron sputtering”, IOP Conf. Series: Materials Science and Engineering 12 (2010) 012004.

[10] Akihiro Ikeda, M. Abd Elnaby , Reiji Hattori, Yukinori Kuroki, “Effect of nitrogen plasma conditions on electrical properties of silicon oxynitrided thin films for flash memory applications”, Thin Solid Films 386 (2001) 111-116.

[11] A. De Vos and D. Van Dhelsen, “The temperature dependence of the electrical properties of thin tellurium films”, Revue De Physique Appliquée. - 14, (1979) 815.

[12] Shinho Cho, Jung Chul-Park, and Cheon Lee, “Current and temperature controlled variable inductance in superconducting microstrip lines”, IEEE Trans. on Appl. Superconductivity 11 (2011) 3090.

[13] X. Zhang, et.al. , “Thermal and electrical properties of a suspended nanoscale thin film”, Intl. J of Thermophys., 28, (2007) 33.

[14] Yoshikazu Yoshida, Katsuyuki Ito, Yasunao Okazaki, Tsuneo Mitsuyu and Shin-Ichi Mizuguchi, “Development and application of a nozzle-beam-type microwave radical source”, Rev. Sci. Instrum. 66, 1015 (1995).

[15] C. L. Tien, A. Majumdar, and F. M. Gerner, Microscale Energy Transport, Taylor & Francis, Washington, DC, 1998.

[16] Youqi Ke, et. al., “Resistivity of thin Cu films with surface roughness”, Phys. Rev. B 79, (2009) 55406.

[17] Majid Mosleh, Nini Pryds, Peter Vang Hendriksen, “Thickness dependence of the conductivity of thin films $(La,Sr)FeO_3$ deposited on MgO single crystal”, Mat. Sc. and Engg. B 144 (2007) 38–42.

[18] Yang-Ming Lu, Chun-Yuan Chen, Ming Hong Lin, “Effect of hydrogen plasma treatment on the electrical properties of sputtered N-doped cuprous oxide films”, Mat. Sc. and Engg. B 118 (2005) 179–182.

[19] P. Dutta, S. Paul, D. Galipeau, V. Bommisetty, “Effect of hydrogen plasma treatment on the surface morphology, microstructure and electronic transport properties of nc-Si:H”, Thin Solid Films 518 (2010) 6811–6817.

[20] M. Lascaud, A. Lachter, J. Salardenne and A. S. Barriere, “Electrical conduction mechanisms in FeF_3 thin films”, Thin Solid Films, 59 (1979) 353-360.