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A Comparative Analysis of Some Models on the Effect of Annealing on the Electrical Conductivity of Metallic Thin Films

U.S. Mbamara* and C.I. Iroegbu
Department of Physics, Federal University of Technology, Owerri, Nigeria.
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Abstract

We have surveyed some models on the effect of annealing on the electrical conductivity of metallic thin films. In both discontinuous and continuous films, annealing largely reduces the number of grain boundaries and increases the specularity of the thin film. In either case, donor impurity assistance and vacancy decline are also respectively enhanced. Allowing for interplay with other extraneous factors, a net suppression of the activation energy for carrier mobility is exhibited, leading to enhanced electrical conductivity in the films.

Keywords: Annealing, Grain boundaries, Specularity, Activation energy, Carrier mobility.

1.0 Introduction

Solid thin films form the basic materials for the study of general structural and physical properties of solids, where special beam methods require only small quantities of materials of extremely thin layers. Examples include transmission electron microscopy and diffraction, neutron diffraction, uv spectroscopy and x-ray diffraction and spectroscopy, among many others. Such effects as the rotational switching of ferromagnetic films, electron tunneling processes, electromagnetic skin effects of various kinds, and certain optical interference phenomena, etc. often arise as a result of the extreme thinness of the material itself, so that thin films furnish the best means of studying the effects (Cambell, 1996). Films are also invaluable for the investigation of nucleation and crystal growth, and for the study of states of extremely distorted thermodynamic equilibrium (Wagendriestel, *et al.*, 1994).

The overall properties of thin films are closely linked with such extraneous factors as the deposition rate, gaseous impurities, substrate structure and temperature (Dash, 1975). Very dramatic changes are observed in amorphous or microcrystalline metal films on substrates cooled to the temperature of liquid helium (4.2K). At such temperature the metal lacks the thermal energy that is needed for extensive diffusion. This results in an extremely disordered structure. In other materials grains, grow gradually as the temperature is raised, with little or no transformation. Such films may have small grains but their structures approach that of the bulk material.

The interaction of the metal film with the substrate leads to the subjects of film nucleation, growth, coalescence and epitaxy. With the use of the low-energy electron diffraction (LEED) technique, it is now known that in some cases uniform crystalline monolayers, or near so, of a metal can be formed on a particular substrate. Especially interesting is the possibility of growing highly epitaxial metallic and semi-conducting superlattices that are periodic structures of atomic size dimensions. Furthermore, ultra thin films furnish a most effective way, and often the only way, for studying certain phenomena of most materials, particularly in approximately two dimensions and at sub-micro levels (Wiki, 2007). The result of such super-high technology studies is the nursing mother of the nanotechnology concept.

2.0 Electron Transfer in Metallic Thin Films

Studies on charge movement in metallic thin films show that they do not occur as straightforward phenomena, as perhaps in the bulk structure. The transfer processes which show up most prominently are thermionic emission, quantum-mechanical tunneling, charge avalanche, ac conduction, photoconduction, autoionisation and electron capture (including Auger effect), ohmic conduction

*Corresponding Author's Email: *uesmbams@gmail.com*

(incorporating surface and grain-boundary scattering) and superconduction (Coutts, 1974). Cottey (1969) stated that in general, the major factors which guide the pattern of conduction in metallic thin films are mostly inherent in the films, and include the deposition pressure (for vacuum- and chemical vapour- deposited films), deposition temperature vis-à-vis substrate temperature, film-substrate absorptivity and adsorptivity, surface effects, grain size and boundaries, point and line defects, film porosity, film thickness, anneal factors, ambient temperature, temperature coefficient of resistance (TCR), thermal activation energy, thermonuclear power, Fermi energy, band gap, existence of traps, sources and sinks, potential barrier or gradient, film anisotropy and epitaxy, permittivity and permeability of film and substrate, plasma frequency and acoustic response, refractive index and photosensitivity, film specularity, eddy current size effect, skin effect (including cyclotron resonance size effects), Hall effect and magnetoresistance. Although the relative effects of most of these factors are combined, thinness and ambient temperature are the key players that determine or modify their extent.

3.0 Conduction Methods

3.1 Conduction in Discontinuous Films

Metallic films are usually discontinuous in their early growth stage, and a continuous bridge for current flow is lacked. At this stage therefore, the conduction mechanism is similar to those of insulating films sandwiched by metal films. As the islands grow, the conductivity of the film is enhanced, the effects of the extraneous factors notwithstanding. When a homogeneous or continuous film is obtained, the effects of some of the listed factors wane, and only those factors generally associated with the electrical conductivity of normal metals, for instance grain size, mean free path, temperature, etc., become significant. Electron transfer between individual particles or islands are itemized into three basic modes viz-quantum-mechanical tunneling, thermionic emission and impurity-assisted conduction. At least two of the mechanisms are known to take place simultaneously in any discontinuous film conduction.

For tunneling, Neugebauer and Webb (1963) proposed a three-particle (island) model and opined that only electrons excited to the order of e^2/r above the Fermi level of a particular island could be transferred to the island (e^2/r being the work done in removing an electron from an island of size r to ∞). For an island of area r^2, their model gives

$$\Pr^2 = Kr^2 DeV \quad ...1$$

transitions per second, each of which takes a time

$$t = 1/Kr^2 DeV \quad ...2$$

where P is the absolute probability multiplication factor, K is a constant having a unit of $(CV)^{-1} m^{-2} s^{-1}$, D is the transition probability, and V is the potential. The average velocity of the electrons is

$$\mathbf{v} = \mathbf{s}/\mathbf{t} = Kr^2 DeV\mathbf{s} \quad ...3$$

(s = separation between adjacent islands), while their mobility is

$$\mu = (s/t)(V/s) = K\mathbf{s}^2 r^2 De \quad ...4$$

The conductivity then is

$$\sigma = n_r e\mu = K\mathbf{s}^2 e^2 D \exp\left(-\frac{(e^2/r)}{kT}\right) \quad ...5$$

where $n_r = n/r^3$ is the density of occupation for an island of radius r, and defined by the factor (Neugebauer and Webb, 1963)

$$n_r = (1/r^2)\exp\left(-\frac{(e^2/r)}{kT}\right) \quad ...6$$

n being the total number of conducting electrons. Thus the Neugebauer and Webb model predicts that conductivity is:

i. inversely proportional to island size r^2;

ii. directly proportional to the square of island separation s;

iii. exponentially dependent on 1/T.

For a transfer between two nearby islands with an applied field in between, the maximized activation energy is given by (Neugebauer and Webb, 1963),

$$\delta E_{\max} = \left(e^2/4\pi\varepsilon_o\varepsilon_r\right) - 2\left(eF/4\pi\varepsilon_o\varepsilon_r\right)^{\frac{1}{2}} + 2rF \quad \ldots 7$$

The first term on the right hand side represents the field potential, the second term the image potential, and the third term a contribution from other intrinsic sources resulting from the image force. This third term is small compared with the first two, so that the activation energy decreases with the square root of the voltage drop between the islands. Hill (1969) later combined the three particle model of Neugebauer and Webb with the more elaborate tunneling theory of Simmons, to arrive at a fine-tuned activation energy for charge tunneling.

For thermionic emission, one can invoke the Richardson-Dushman equation to express the net current density between two adjacent islands as (Coutts, 1974)

$$J = AT^2\left(eV/kT\right)\exp\left(-\varphi/kT\right) \quad \ldots 8$$

where A is the island area, V is the potential and φ is the metal-insulator work function. For a field of say 100V/m applied to a film of islands of 20 Å diameter and same separations, the average voltage drop between the islands will be about 4x10"7V. Thus for a barrier height of 0.5 eV, the current density at room temperature will be approximately $10^{-11}\,Am^{-2}$, which is sufficiently large for thermionic emission to occur. By analogy with the theories of activated tunneling one appreciates that the barrier height in the last equation includes a term representing the energy dissipated in moving a charge from one island to the next. To compare the theories of tunneling and thermionic emission, van Steensel (1967) constructed a diagram of electrode separation against barrier height for tunneling and thermionic emission (Figure 1).

If one considers the case of electrodes having a potential barrier of 0.1eV and separated by gaps greater than 20Å, then at 200K conduction should occur by thermionic emission. But for a barrier of less than 20 Å, transfer will most probably take place by tunneling. Hill (1969) repeated the process for island films and his result is shown in Figure 2, with the activation energy term included for comparison.

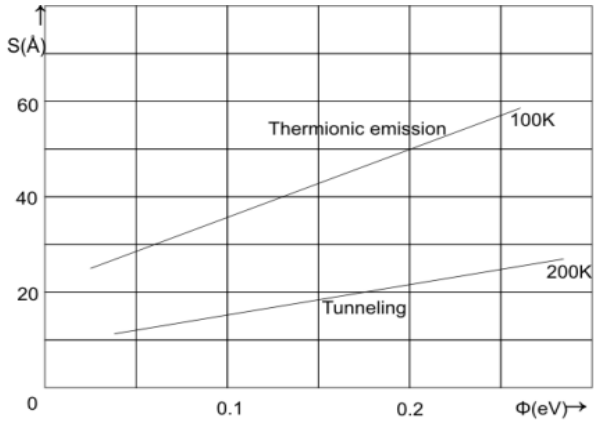

Figure 1: Electrode separation versus barrier height. In the regions above the curves, thermionic emission dominates the conduction process whilst below the curves, tunneling is the most probable mechanism (after van Steensel, 1967).

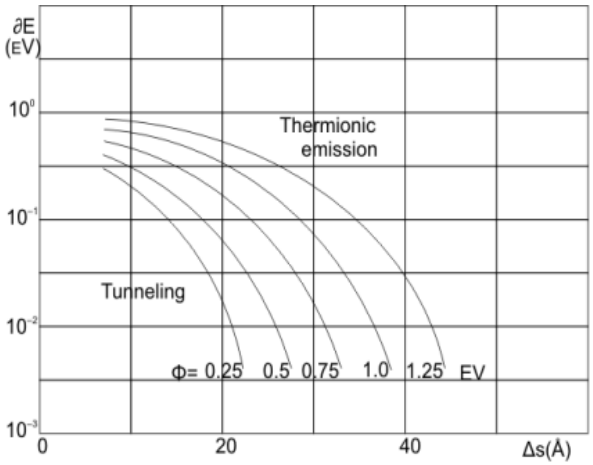

Figure 2: Activation Energy versus reduced particle spacing (after Hill, 1969).

Wei (1963) studied the electrical properties of ultrathin films of potassium deposited on potassium chloride substrates and observed an activated process. To explain this result he invoked the theory of impurity conduction developed by Mott and Twose (1961) and by Miller and Abraham (1960). The latter authors opine that the activation energy for impurity conduction is given by

$$\delta E_{\max} = \left(e/\varepsilon_o\varepsilon_r r\right)\left[\left(4\pi N_d\right)\left(1-1.35K\right)\right]^{1/2} \quad \ldots 9$$

where $K = N_a/N_d$ is called the compensation ratio, N_a and N_d being the acceptor and donor densities respectively. The electrostatic energy needed for tunneling is (Price, 1957)

$$\delta E_{\max} = \left(e/4\pi\varepsilon_o\varepsilon_r\right)\left(1/r_{ad} - 1/r_{aa}\right) \quad \ldots 10$$

where r_{ad} is the separation between donors and r_{aa} is the separation between acceptors.

Some other authors have proposed a model which leads to virtually the same result as that of Neugebuauer and Webb, but based on a rather different conception of the conduction mechanism and of the activation energy involved (Wiki, 2007). They suggest that the absorption of a phonon is necessary before an impurity-assisted jump can occur. The hypothesis however, is not fully developed. On another note, the anomalously high currents observed in metal-insulator-metal (MIM) structures are linked with inter-island trap models by some authors; but in virtually all such cases no mention is made of the possible effect of barrier width by image forces, although for widths in excess of about 20 Å this would be negligible. The fore-going furnish that the hopping process between different energy levels in an activated process is of the form

$$\sigma(T) \propto \exp\left(-E/kT\right) \quad ...11$$

with the activation energy E dependent on the density and distribution of traps.

3.2 Conduction in Continuous Films

The main factors that affect electron movement in continuous films include surface scattering, grain boundary scattering, angular dependence of the specularity parameter, and such other inter-playing factors as the size effect.

Thomson (1920), invoking the Drude-Lorentz theory, formulated the concept of surface scattering and the effect of thickness on conductivity by calculating the mean value of all the possible mean free paths of an electron. But Fuchs (1938) subsequently criticized the model for its inconsistency in formulating the mean free path, and went ahead to analyse the size effect by solving the Boltzmann transport equation with appropriate boundary conditions. Lucas (1964) extended Fuchs' analysis to allow for specularity parameters at two film surfaces. Campbell (1966) eventually calculated the resulting functions in terms of the film resistivity and got results which are in reasonable agreement with experiments. Still on the ensuing developments, Mayadas and Shatzkes (1970) formulated a model which, although grossly over-simplified, made some qualitative predictions about the scattering to be made. An analysis of the effect of grain boundary scattering on film resistivity using their model is shown in Figure 3.

The effect of specular reflection on the conductivity of metallic thin films is inter-woven with the other factors already discussed, as is the size effect, and these are considerably reflected in the preceding paragraphs. The activation energy for conduction is affected in much the same way by these factors as the others and actually imbedded with them.

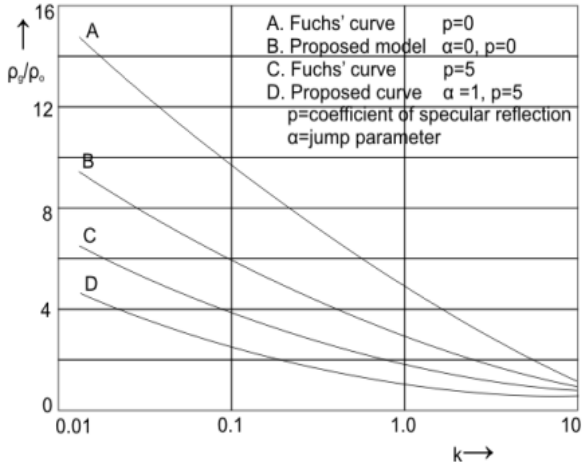

Figure 3: The effect of grain boundary scattering on film resistivity (k = film thickness over mean free path (after Mayadas and Shatzkes, 1970).

4.0 Annealing and Its Impact on The Conductivity of Thin Films

Annealing generally falls into the technology of heat treatment and varies with materials and their intended end uses. For metallic thin films, Coutts (1974) stated that annealing does not refer to changes in film structure due to grain growth, as in the bulk material, but to the removal of defects from the structure. Dobson and Hopkins (1968) carried out annealing experiments on W films and showed that the activation energy of very thin films decreased after annealing.

For island films of average size r and separation s, the volume of the islands per unit area is

$$V = \frac{2}{3}\frac{\pi r^3}{(2r+s)^2} \quad ...12$$

granted that the resolved volume of an island of average radius r is $(2/3)\pi r^3$, while the allotted area is $(2r+s)^2$. Hence,

$$s = \left(2\pi r^3 \big/ 3V\right)^{1/2} - 2r \qquad ...13$$

and

$$\frac{ds}{dr} = \frac{3}{2}\left(\frac{2\pi}{3V}\right)^{1/2} r^{1/2} - 2 \qquad ...14$$

which upon inserting equation (12), becomes

$$\frac{ds}{dr} = \frac{2r+3s}{2r} \qquad ...15$$

Stemming from the Coulomb force-field within islands of resolved separations, $\left((r+s)/r(2r+s)\right)$, the work done in charge transfer from one island to the next is

$$\delta E = \left(e \big/ 4\pi\varepsilon_o\varepsilon_r\right)\left((r+s) \big/ r(2r+s)\right) \qquad ...16$$

so that,

$$d\left(\frac{\delta E}{dr}\right) = \left(\frac{e}{4\pi\varepsilon_o\varepsilon_r}\right)\times \left(\frac{\left(r(2r+s)-(r+s)(4r+s)\right)}{r^2(2r+s)^2}\right) = \frac{-e(2r^2+4rs+s^2)}{4\pi\varepsilon_o\varepsilon_r r^2(2r+s)^2} \qquad ...17$$

and

$$d\left(\frac{\delta E}{dr}\right) = \left(\frac{e}{4\pi\varepsilon_o\varepsilon_r}\right)\frac{\left(r(2r+s)-(r+s)r\right)}{r^2(2r+s)^2} = \frac{e}{4\pi\varepsilon_o\varepsilon_r(2r+s)^2} \qquad ...18$$

This implies that the change in activation energy will be negative if

$$\frac{2r^2+4rs+s^2}{r^2(2r+s)}dr > (2r+s)^2\,ds \qquad ...19$$

That is, if

$$\frac{ds}{dr} < \frac{2r^2+4rs+s^2}{r^2} \qquad ...20$$

This expression for ds/dr shows that the condition for a negative change of activation energy upon annealing is

$$\frac{2r+3s}{2r} < \frac{2r^2+4rs+s^2}{r^2} \qquad ...21$$

or, upon rearrangement of equation (21),

$$2r^2+5rs+2s^2 > 0 \qquad ...22$$

Since r and s are both greater than zero the inequality is always true. One then concludes that the change in activation energy upon annealing is always negative, irrespective of the initial sizes and separations.

For continuous films, early investigations were initiated by the observation that the resistance of a film decreased irreversibly when heated beyond the deposition temperature, and spontaneously even when held at a constant temperature immediately after deposition. To analyse the decrease in resistance with temperature, Vand (1942) first considered the possible defects that were responsible. These were lattice vacancies, interstitials, and combined vacancies and interstitials. He made five assumptions which helped him to develop a mathematical basis for his notion on film resistivity cum annealing. This led him to an expression for the characteristic function as

$$F(E_o(t)) = -\left(\frac{dR}{dt}\right)\left(\frac{1}{kU}\right) \qquad ...23$$

where R_i is a characteristic parameter referring to point defects, k is Boltzmann constant, and $U = u(u+2)/u+1$ with $u = E/\alpha t$ and α equal to the rate of temperature increase. Dexter (1952) from his own work concluded that vacancies and interstitials each caused an additional resistivity of $0.4 - 4.3\times10^{-6}$ Ωcm/at. %. Thus conductivity increases as the number of vacancies reduces, as in a typical anneal process.

Impurity assistance to conductivity will depend on the type of impurity. While Sugihara (1984) insists that in general impurity-assisted hopping is temperature-independent at low temperatures, Roche *et al.* (1990) discovered that at such temperatures, conductivity may be enhanced by the introduction of shallow donor impurities close the

centre of n-layers. Otherwise phonon scattering would predominate (Sugihara, 1984), leading to reduced conductivity. Here, and for the presence of vacancies, annealing comes to play from the findings of Kuznetsov & Svensson (1999). They discovered, after some artificial introduction of vacancies, that upon annealing there is a preferential formation and subsequent dissociation of high-order vacancy clusters. With the elimination of such vacancy clusters, impurity separation would be reduced and conductivity is enhanced. Combining these later findings with Vand's derivation leads us to some irreversible changes upon the annealing of metallic thin films. The net effect of such changes is a decrease in the electrical resistivity (i.e. increased conductivity) of the films, as shown in Figure 4.

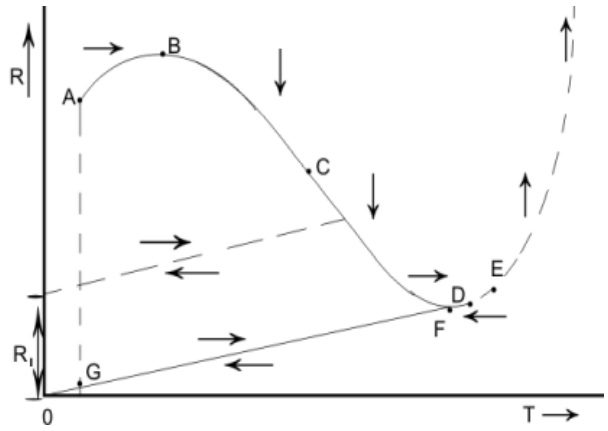

Figure 4: Irreversible changes in resistance of metal film with temperature (after Vand, 1968).

Along the region AB, resistance follows a near-straight line. Somewhere in the region of B, the deposition temperature, the resistance begins to decrease as defects are annealed out. If the temperature is then decreased from any point on the curve BD, the resistance will follow a straight line almost parallel to AB, and will cross the resistance axis at a point R_i. This represents the contribution to the resistance of defects, etc. Of course not all defects can be annealed out, but at a point such as D, $R_i=0$.

Gas molecules adsorbed during film deposition act as impurity scatterers of conduction electrons. However, the results emanating from adsorption studies tend to be rather confusing. The mechanisms which have been used to explain the changes include chemisorption, physisorption and diffusion adsorbed layers into the film structure (Santhosh, *et al*., 2002; Wiki, 2010). Majority of the work on adsorption has been carried out using oxygen, whilst the effects of other gases have been studied to a lesser extent. But here still, spontaneous decay in resistance is observed upon annealing. With the introduction of oxygen and subsequent annealing, stability in resistance is achieved, implying the inhibition of the annealing process by the adsorbed oxygen. The reason however is unclear. The annealing of films before exposure to nitrogen results in smaller increase in resistance.

Cyclic curves are often obtainable upon the annealing of a typical metal film. At low temperatures (~5K) the resistance decreases irreversibly with reproducible cooling cycles which depend on the maximum annealing temperature attained in the previous cycle. Annealing at further elevated temperature (~150K) produces nearly bulk-like value of the resistance, which however, continues to decrease with further annealing at higher temperatures. The superconducting transition temperature decreases with successively increasing annealing temperature, attaining nearly bulk values at peak temperatures (Wiki, 2007).

5.0 Conclusion

Through this extensive survey and analysis we have established that island film conductivity depends on island size, island separation and temperature. For continuous films, grain size, vacancies, impurities and specularity constitute the major factors to conductivity. In all, the activation energy is lowered upon annealing, for the simple fact that grain growth occurs and vacancies expunge, with donor atoms getting closer to the acceptors. Inherent stresses relax upon annealing and some island films coalesce. As grain growth occurs, more uniformity is achieved and film epitaxy increases. In each case, the conductivity of the thin film is naturally enhanced.

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