The evolution and analysis of electrical percolation threshold in nanometer scale thin films deposited by electroless plating

V. Sabayev*, N. Croitoru, A. Inberg, Y. Shacham-Diamand

Department of Physical Electronics, Faculty of Engineering, Tel Aviv University Ramat Aviv, Tel Aviv 69978, Israel

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1. Introduction

Initial researches of conduction threshold in mixtures of conducting and nonconducting materials are belonged to early 1960s. The first mathematical formulation of classical threshold has been introduced by Broadbent and Hammersley [1]. It is one of the simplest models exhibiting a phase transition and the occurrence of a critical phenomenon is central to the appearance of percolation. From a mathematical point of view percolation is attractive because it exhibits relations between probabilistic and algebraic/topological properties of different systems.

Electrical conduction thresholds in disordered mixtures of conducting and nonconductive materials have been firstly observed by studying the mixtures of silver balls and bakelite powder when disorder may be introduced in a variety of ways [2]. The most common statistical assumptions are known as “bond percolation” and “site percolation” models [3–5]. In the first case some known fraction of the bonds distributed randomly, are missing from the system while in the second known fractions of sites are assumed to be missing.

In general, topological aspects of percolation threshold have emerged from the work of Dean and Bird [6]. Quantities relevant to percolation threshold are defined in the limit $N \to \infty$, where $N$-number of the sites in percolating system which depend on $x$, the concentration of allowed sites within the system and its geometry. When the concentration of allowed sites is lower than some critical value $x < x_c$, these sites occur singly or in a small isolated clusters. As $x$ increases, larger clusters can be formed and the mean size of the cluster is growing. When $x$ approaches $x_c$, the larger clusters begin to merge creating a few extremely large clusters along with a fewer small ones. The ratio of number of the sites in this large cluster to the number of sites in the system is defined as site percolation probability $P^{(s)}(x)$. For $x > x_c$ the infinite cluster grows rapidly absorbing smaller clusters. Correspondingly $P^{(s)}(x)$ rises sharply from zero just above threshold and goes asymptotically to $x$ when $x > x_c$ and isolated clusters become rare. Therefore $P^{(s)}(x)$ near threshold can be characterized by simple power law:

$$P^{(s)}(x) \propto (x - x_c)^{-n}$$

(1)

It should be noted that two percolation thresholds can be detected contaminations or oxidation states. The strong dependence of the film surface roughness on metal ion concentration in solution was observed while the deposition rate and the resistivity remain unaffected.

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re-aggregation, and as a result, conducting network formation can take place at lower concentration. Particle movement can be caused by diffusion, convection, shearing or external fields. Statistical percolation refers to a situation where randomly distributed filler particles form percolating path. Since the early observation of percolation-dominated electrical conductivity in an insulator-conductor system a power-law behavior appears in most cases [7] with a maximum which depends on system parameters. The general model which defines electrical properties of percolated system is Resistor Network Model [8]. According to this model, if the spatial arrangements of conducting and non-conducting materials within the system are known and all dimensions of the conducting regions are large with respect to electron mean free path, a local resistivity can be defined by the bulk value of the resistivity found at some reference point.

As a result of rapid development in materials engineering and nanotechnology the percolation phenomenon was transferred to nanoscale. Electrical percolation in mixtures of electrically conducting and nonconducting nano materials is widely investigated [9,10]. It can be revealed that control of percolation threshold is very significant for different microelectronic applications because it allows controllable exhibition of two opposite states at any system. In case of electrical resistivity this can be transition from the insulating to conducting state. Such transition at percolation threshold is extremely important for electrical contacts and interconnects metallization for integrated circuits where thickness and electrical conductivity are main figures of merit of the deposited metal films [11]. Comparatively to other metals silver (Ag) and copper (Cu) thin films possess very low specific bulk resistivity of 1.59 μΩ cm and 1.68 μΩ cm, respectively [12] and, therefore, are intensively used in ULSI metallization technology. Obviously, a proper deposition method is one of the key parameters for obtaining high quality films. The widely used in microelectronics are Atomic Layer Deposition (ALD) and different sputtering techniques like DC and reactive sputtering. Along with numerous advantages different limitations are constraining the implementation of this methods. The major limitation of ALD is its slowness. Usually only a fraction of a monolayer is deposited in one cycle. The main disadvantage of the sputtering method is its incompatibility with a lift-off process for the film structuring because of diffusion transport. Thus, undesired diffusion can lead to contamination problems [13]. Among different thin metal films’ deposition methods with desired properties and quality, the electroless deposition (ELD) was found as very effective for interconnect metallization and various microtechnology applications [14]. In comparison to most other methods ELD is relatively simple, low cost, offers high selectivity and enables self-aligned deposition, hence saving photolithography steps. ELD is also very versatile and can produce many metals and alloys with good quality on high aspect ratio vias and trenches. Therefore, ELD offers valuable solutions to industrial and research issues and is a matter of interest from both practical and theoretical perspectives. Moreover, control and reversibility of electrical transport in electroless deposited thin films at percolation threshold can be implemented in different devices. Resistive switching memories, sensors, actuators and thin film transistors can exploit transition at percolation threshold as a basic feature [15-17].

In this work we have concentrated our detailed study on the impact of morphological and physical parameters of ELD Ag and Cu thin films at percolation threshold in order to provide the basis for the new and more advanced electronic devices and materials. Analysis of the resistivity at percolation threshold has been performed. A basic explanation of percolation threshold evolution and its influence on Ag and Cu thin film resistivity has been proposed. Influence of the ELD parameters on percolation threshold and total thin film resistivity has been analyzed.

2. Experimental setup and methods

Silver (Ag) and copper (Cu) thin films were prepared by electroless deposition at the same temperature of 5.55°C for 1.5 cm silver and copper cleaned ultrasonically for 30 min in acetone and isopropanol, respectively, with followed treatment in chromous sulfuric acid (H2SO4 92%, CrO3 1.3%) at 80°C for 1 h to remove all organic and inorganic residues. After each cleaning step the samples were thoroughly rinsed by deionized (DI) water with 18 MΩ resistivity and dried by nitrogen flow. All chemicals used were purchased from Sigma–Aldrich. Silane-based amino-terminated self-assembled monolayer (SAM) was used as adhesion promoter. Typically, thickness of the SAM is determined by the length of the precursor molecules and an adsorption angle of the molecules and lies within 1–2 nm. In this work a 2% aqueous solution of 3-aminopropyltrimethoxysilane (APTM) was used. The silanization of the substrates was thoroughly rinsed by DI water and dried by nitrogen flow. To provide self catalytic deposition of Ag and Cu thin films on SAM, the surface before metallization was activated by wet treatment in a home made aqueous palladium colloidal solution containing [M]: PdCl2—0.005, SnCl2·H2O—0.2, KCl—1.9 and HCl—1.6, at room temperature for 10 min. Ag and Cu thin films were deposited on activated SAM at room temperature from proper base electrolytes. Back surface of the samples was isolated by protective layer to prevent metal deposition. Ammonia acetate solution of the content [M]: AgNO3—0.05, NH4OH (25%)—1.83, CH3COOH—0.08, and hydrate-hydrate as reducing agent—0.1, at pH 10.5 was used for Ag ELD. The Cu ELD was performed from tetratrate/formaldehyde bath containing [M]: CuSO4·5H2O—0.08, KNa-tetratrate—0.35, NaOH—0.5, Na2CO3—0.14 and formalin (38%) as reducing agent—0.67, at pH 12.5–13. All metal films passed adhesion tests using Scotch tape peeling.

To identify electrical and physical properties of ELD thin metal films different characterization methods were used. The thickness and roughness (RMS) of the deposits were measured by Atomic Force Microscope (AFM) Multimode Scanning Probe Microscope, Digital Instruments Inc., USA. This unit was able to provide images from the atomic scale up to 5 μm. Commercially available Ti-Pt/50 ultra-sharp Si tips produced by MicroMasch, Spain were used for all measurements. The composition of the films was determined by X-ray Photoelectron Spectroscopy (XPS). The measurements were performed in ultra-high vacuum, 2.5 × 10−10 Torr base pressure, using 5600 Multi-Technique System (PHI, USA). The samples were irradiated with an Al Kα monochromated source (1486.6 eV) and the outcome electrons were analyzed by a Spherical Capacitor Analyzer using the slit aperture of 0.8 mm, charging the samples with 50 μC.cm−2. Spectrum was scanned from a wide energy range from 0 to 1400 eV at low resolution 187.85 eV pass energy and at high resolution 11.75 eV with 0.05 eV step. High resolution measurements allow precise energy position and peak shape determination which is necessary for bonding analysis. The resistivity of the samples was measured by In-line Four Point Probe (PPP) Resistivity Tester, Model 301-6, Sigma-Tau, USA. The PP3 setup was assembled from equally spaced tungsten metal tips with finite radius. Each tip was supported by spring on the end to minimize the sample damage during probing. The four metal tips were the part of auto-mechanical stage which traveled up and down during measurements. The high impedance current source was used to supply current to determine the sample resistivity. Typical probe spacing was 2–3 mm. To observe thin film morphology and microstructure Scanning Electron Microscope Quanta 200 FEG Environmental Scanning Electron Microscope (ESEM) was used. The ESEM can be switched between different vacuum modes enabling the investigation of conductive at high vacuum typically ≤10−3 mbar and non-conductive at low vacuum ≤1 mbar. Pressure of the range of the sample voltage was from 200 V to 30 kV with available resolutions ≤2 nm at 30 kV in high vacuum and ≤5 nm at 3 kV in low vacuum mode at beam current more than 100 nA.

3. Results and discussion

In case of ELD activation of the dielectric surface by the catalyst is extremely important for following metallization. Homogeneous seed layer can provide high quality film with improved electrical properties. To visualize the effectiveness of the glass surface activation after wet treatment in palladium solution standard AFM methods such as roughness and bearing analysis were used. Bearing analysis provides additional information beyond standard roughness measurements by revealing how much of a surface lies above or below a given height. Surface roughness is generally represented in terms of statistical deviation, root mean square (RMS), from average height. However, this gives little indication of height distribution over the surface. Bearing analysis determines what percentage of the surface (the “bearing ratio”) lies above or below any arbitrarily chosen height. A bearing ratio of 100% corresponds to 100% of the surface lying above a given surface height. The samples were analyzed for different exposure times in activation
solution. The RMS values of 2.95 nm, 1.81 nm, 1.05 nm and 0.94 nm for 30 s, 120 s, 600 s and 1 h of exposure time, respectively, were observed. The initial RMS value of the substrate before Pd activation was 6.67 nm. It should be noted that RMS value after overnight exposure of the samples in activation solution was the same as after 1 h.

Consequent decrease of RMS with increasing exposure time was confirmed by bearing analysis (Fig. 1). Distribution of surface height over the sample decreases with exposure time and reaches the lowest value at highest exposure time. When the coverage is dense enough the saturation somewhere about 1 h of exposure time is reached [18]. As a result dense and homogenous surface coverage by catalyst is obtained for following ELD of Ag and Cu thin films.

The growth kinetics of Ag and Cu thin films were observed by ESEM and presented in Fig. 2.

The thin films can be considered as percolating system of disordered metal clusters deposited on dielectric substrate. Most metals do not wet insulating surfaces and in such case, during the growth, thin film passes through a sequence of morphological changes as the film thickens. When sufficiently thin, the film consists of isolated compact islands which as more material is deposited, grow and coalesce into larger, but still compact islands. At some critical film thickness, islands that touch no longer fully coalesce into near equilibrium compact shapes. As deposition proceeds, this shapes stop to growth forming percolating structure. Finally the channels between the structures are filled in and a continuous, hole free film is created. It should be noted, that there is a difference in growth modes of Ag and Cu films. It is generally accepted that there are three possible modes of thin film growth on the surfaces [19]. In particular there are the island mode, or Volmer–Weber mode, small clusters are nucleated directly on the substrate surface and then grow into islands of the condensed phase. This happens when the atoms or molecules of the deposit are more strongly bound to each other than to the substrate. This mode is exhibited by many systems of metals growing on insulators, including many metals on alkali halides, graphite and other layer compounds such as mica. The layer mode, or Frank–van der Merwe mode, displays the opposite characteristics. Because the atoms are more strongly bound to the substrate than to each other, the first atoms form a complete monolayer on the surface, which becomes covered with a some-
The influence of the metal concentration in solution on Ag and Cu thin film growth kinetics (Fig. 3) was studied together with thin film growth modes [20–22]. Therefore Cu thin films clusters coalesce at lower thickness than Ag clusters and percolation structure of Cu thin film can be reached faster and at lower thickness.

The Ag and Cu thin film thickness as a function of deposition time and ELD bath composition.

![Graph showing film thickness as a function of deposition time](image)

**Fig. 3.** The Ag and Cu thin film thickness as a function of deposition time and ELD bath composition.

what less tightly bound second layer. Providing the decrease in binding is monotonic, toward the value for a bulk crystal of the deposit, the layer growth mode is obtained. This growth mode is observed in the case of adsorbed gases, such as several rare gases on graphite and on several metals, in some metal–metal systems, and in semiconductor growth on semiconductors. The layer plus island mode, or Stranski–Krastanov growth mode, is an interesting intermediate case. After forming the first monolayer or a few subsequent layers, growth as a layer is unfavorable and islands are formed on top of this intermediate layer. It was observed that growth of Ag thin films defined by Stranski–Krastanov and Cu by Volmer–Weber growth modes [20–22]. Therefore Cu thin films clusters coalesce at lower thickness than Ag clusters and percolation structure of Cu thin film can be reached faster and at lower thickness.

The influence of the metal concentration in solution on Ag and Cu thin film growth kinetics (Fig. 3) was studied together with roughness measurements. The content of metal ions was varied by dilution of the base solutions by DI water to the ratios of 1:10, 1:6 and 1:3 named as low, medium and high concentration, respectively. It should be noted that pH of the electrolyte was not affected by dilution and remains at the order of 9 ± 0.5 and 13 ± 0.5 for Ag and Cu solutions, respectively.

The variations of the film roughness as a function of deposition rate can be extremely important for the thin film quality and possible application of ELD thin films. It was observed that for both Ag and Cu thin films, in spite of initially high deposition rate of Ag film, roughness varies weakly for low and significantly for high metal concentrations. At percolation threshold for Ag thin films RMS remains at the order of 4.3 nm for low concentration and varies from 4.3 nm to 13.7 nm at high concentration. Similar results were obtained for Cu thin films. At percolation threshold RMS remains at the order of 6.3 nm at low concentration and varies from 6.3 nm to 13.9 nm at high concentration. However, deposition rate remains approximately constant with small deviations for both metals. The main difference appears in incubation period, which changes strongly for Cu and remains almost constant for Ag films. Therefore, the roughness fluctuations cannot be explained by different deposition rate only. The deposition rate can be considered as a main factor responsible for the formation of less ideal structure with higher roughness but the influence of additional parameters of ELD on the film surface roughness should be analyzed. This observation can be central for different microelectronic applications where surface roughness can allow or restrict subsequent surface treatment or lithography steps.

The electrical resistivity ($\rho$) behavior at percolation threshold, as one of the key parameters at nanoscale metallization, of ELD Ag and Cu thin films was analyzed. The electrical percolation threshold can be defined as the filler volume fraction at which the measurements begin to show percolation behavior. In other words, this is the critical fraction of sites in percolating system that must be filled by conductor to create a continuous path of nearest neighbors from one side to another one, i.e. that at the percolation threshold the material becomes highly conductive. The most interesting point is the region just below percolation threshold where the neighboring sites are still quite densely packed but separated by narrow gaps of insulator. These networks represent a class of conductors that are neither classically metallic nor a classic dielectric and offer a lot of unique properties relevant to practical applications. The variation of system parameters like synthesis method, treatment, dimensionality as well as filler type may allow fine tuning of percolation threshold, however, a thorough understanding of process is required. In our case the system of ELD Ag and Cu thin films on dielectric substrate can be considered as metal conducting clusters divided by empty dielectric gaps. The continuity of the film or gap size is controlled by the thickness with a respect to growth mode of each metal, respectively.

The Four Point Probe (FPP) resistivity measurements of ELD Ag and Cu thin films are presented in Fig. 4a. Thin films with a thickness lower than 20 nm demonstrate high initial resistivity.

![Graph showing FPP resistivity measurements](image)

**Fig. 4.** FPP resistivity measurements (a) and roughness variation (b) as a function of thickness of ELD Ag and Cu thin films. Significant resistivity drop to the values of 2.5 $\mu\Omega$ cm for Ag and 4.3 $\mu\Omega$ cm for Cu at the saturation region can be observed. At the vicinity of electrical percolation threshold resistivity starts to drop at the film thickness of 30 nm and 20 nm for Ag and Cu, respectively. Three distinct regions can be distinguished at resistivity variations: insulator, transition and saturation regions. Within transition region the roughness remains constant (b).
The resistivity of 2.5 $\mu\Omega$ cm for Ag and 4.3 $\mu\Omega$ cm for Cu, near to the pure bulk resistivity values, were obtained for films of 60 nm and 50 nm thicknesses, respectively. For thin films prepared from the solution with different metal concentrations insignificant resistivity fluctuations of $\pm 0.02\%$ were observed. In comparison to Ag, the electrical percolation threshold at lower film thickness was obtained for Cu what strongly correlates with growth dynamic of Ag and Cu thin films. The Cu film covers larger substrate area at lower thickness that allows resistivity drop appearance at approximately 20 nm while for Ag this occurs only at 30 nm. For each metal the resistivity reaches saturation at some critical thickness and further thickness increase does not influence resistivity. The resistivity reduction takes place since electrical transport in percolating system occurs through many parallel conducting channels. The number of the channels increases continuously with increasing film thickness (Fig. 2). The thickness dependence on resistivity observed in thin films exhibits characteristic power law at percolating system [23,24] and can be described by simple relation: 

$$\rho = \rho_{\text{bulk}} \left[ 1 - \left( \frac{3}{2k} \right) \left( 1 - p \right) \int_1^{\infty} \left( \frac{1}{t^2} - \frac{1}{r^2} \right) \frac{1}{1 - e^{-kt}} \, dt \right]$$

(2)

where $k$ is the ratio between film thickness $t$ and electron mean free path $\lambda_0$. Completely phenomenological parameter $p$ is defined as probability that an electron will be specularly reflected upon scattering from the film surface. The second one is Mayadas–Shatzkes [27] grain boundary scattering which described by the relation:

$$\rho = \rho_{\text{bulk}} \left[ \frac{1}{3} \left( \frac{1}{t} + t^2 - t^3 \ln \left( 1 + \frac{1}{t} \right) \right)^{-1}, \quad t = \frac{\lambda}{D} \frac{R}{1 - R} \right]$$

(3)

where $R$ is grain boundary reflection coefficient, $D$ is the mean grain size. When the electron mean free path is the same order as the film thickness the scattering on the thin film edges takes place. When the film thickness reaches values larger than the electron mean free path scattering on the film walls does not affect resistivity anymore and only film ideality has an influence on electrical transport. The electron mean free path of Ag and Cu bulk at room temperature is 52 nm and 39 nm, respectively [28]. If consider the system as 2D and the resistance of the system is finite the variations of resistivity can be determined by morphological factors only, i.e. by appearance of conducting path of different thickness between metal clusters. In this case the resistivity can be described by Fuchs–Sondheimer relation since the first resistivity drop was measured at the thicknesses very close to electron mean free path for both metals (Fig. 4a). At following deposition electron mean free path becomes much smaller compared to film thickness and Fuchs–Sondheimer mechanism becomes less dominant. It is possible to assume that at this phase Mayadas–Shatzkes grain boundary scattering becomes dominant factor. In this case hole free, homogeneous films are formed (Fig. 2c and f). Electric transport occurs mainly within the bulk and resistivity is determined by grain boundary scattering in thin film. At this stage $\rho$ reaches the saturation value (Fig. 4a) at the thicknesses of 60 nm and 50 nm for Ag and Cu, respectively. It should be noted, that...
within insulator–conductor transition region at the thicknesses of 35 nm and 30 nm for Ag and Cu films, respectively, RMS remains constant. Therefore, scattering on the film walls remains unaffected and resistivity change can be associated with percolation mechanism.

In addition chemical composition of the ELD Ag and Cu thin films was analyzed by high resolution XPS. All samples were uncharged during measurements and analyzed at the surface and after sputter cleaning for 1 min with a sputtering rate approximately 15 Å min⁻¹. Results of XPS atomic concentration measurements are presented in Table 1.

Significant carbon and oxygen contaminations were detected at the surfaces of ELD Ag and Cu films. After sputter cleaning amount of carbon decreases to negligible values while the oxygen content remains high enough for both films. This phenomenon was previously observed in ELD Ag and Cu [29,30] films and most likely suggests the presence of deep nano-defects or open nano-pores than the oxides contamination. This suggestion is in a good agreement with Ag3d and Cu2p peaks detected by high resolution XPS analysis (Fig. 5a and b) where no peaks attributed to metal oxide contaminations were determined [31]. Moreover, the appearance of dark spots on the ESEM images of 60 nm Ag and 50 nm Cu films (Fig. 2e and f) and their surface coverage, about 92% and 94%, respectively, clearly indicate the film porosity caused the electron scattering. Therefore, the obtained resistivities can be attributed to the presence of the open pores and demonstrate values of 1.5–2 times higher then the pure metal bulk resistivity.

4. Conclusion

The evolution of percolation threshold in electroless deposited Ag and Cu thin films has been studied and ELD as a method for controllable percolation has been analyzed. Different process parameters were considered in order to understand resistivity behavior at percolation threshold. It was shown that surface activation by Pd nanoparticles prior to metallization allows homogeneous coverage that reaches saturation. Surface metallization by ELD Ag and Cu allows fine tuning of electrical properties of deposited film. It was observed that Ag and Cu thin films reach percolation threshold at the thicknesses of 35 nm and 30 nm and demonstrate resistivity values of 2.5 μΩ cm and 4.3 μΩ cm at saturation stage, respectively. The resistivity values higher than the pure metal bulk resistivity can be associated with the thin film nano-porosity.

At percolation threshold film roughness is constant, therefore, scattering on film walls remains unaffected and resistivity change can be associated with percolation mechanism. It has been shown that the film resistivity varies according power law. The critical exponents of 0.95 and 1.04 for Ag and Cu, respectively, were extracted. The basic explanation of resistivity variation during film growth according to existing models was proposed. The strong dependence of the film surface roughness and incubation period on metal ions concentration in solution was observed while the deposition rate and resistivity remain unaffected. The XPS analysis has not shown contaminations and oxidation states in ELD Ag and Cu films. Moreover, ELD can be used as a method for controllable deposition of metal thin film at percolation threshold. The study of electrical percolation threshold in conductor–insulator transition region can be exploited in different devices and technologies in modern microelectronics.

References