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Annealing influence on electrical transport mechanism of electroless deposited very thin Ag(W) films

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Abstract

Morphology and conductivity (σ) of the non-tarnishing electroless Ag(W) films for interconnect were studied as a function of thickness (d) by Atomic Force Microscopy (AFM) and Tunneling Atomic Force Microscopy methods. For $d \leq 100$ nm the conductivity dependence on thickness can be modeled as percolation of the electrical transport while for thicker $d > 100$ nm layers it was independent on d ($\sigma = \sigma_0$). A simple electrical circuit model that described the experimental dependence $\sigma(d)$ for both thin and thick layers was proposed. The AFM study has shown that the small network changes in the film morphology, due to vacuum annealing cause the significant (few orders of magnitude) improvements in electrical conductivity. Although, near bulk conductivity was achieved for the thicker sample, vacuum annealing was not sufficient to achieve such conductivity for very thin Ag(W) films.

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1. Introduction

The ongoing down-scaling trend of interconnects critical dimensions for both integrated circuits and packaging applications faces many technical and scientific challenges. Among those challenges we can count reliability issues, patterning, heating and circuit design problems that are due to the increase in line resistance per unit length. Currently Al and Cu are used for Ultra-Large-Scale-Integration (ULSI). However recently, in Integrated Circuit Technology Ag has been proposed as the interconnect metal due to its higher conductivity ($\sigma_{\text{bulk}} = 6.5 \times 10^5$ $[\Omega \times \text{cm}]^{-1}$) [1] compared to all other known metals. Although Ag thin film deposition methods are available, there are some unique problems in using pure silver: a. it corrodes and tarnishes in air or in the presence of sulfur [2] and water; b. it has weak adhesion to most dielectric materials, including SiO_2 [3], and c. it diffuses rapidly into silicon [4], inducing increased junction leakage and threshold voltage instabilities. Therefore, thin films of pure Ag require use of capping and barrier layers for integrated circuits interconnect applications. Several schemes to overcome silver main problems have been proposed [5–8]. For example, Ag wires were encapsulated using Ag–Ti alloy or Ag/Ti (Al or Cr) bilayers [5–7]. Other authors have obtained non-tarnishing Ag alloys with Cu and Ge [8]. Although those solutions may work they are either too complicated or expensive.

Thin films of Ag with a small amount of tungsten (Ag(W)) ($\leq$3 at.%) were proposed as reliable and low-resistivity metallization for microelectronic applications. Such films were prepared by electroless deposition technology and their material and electrical properties were studied [9–12]. The σ values of $\sigma \cong 5 \times 10^5$ $[\Omega \times \text{cm}]^{-1}$ for Ag(W) films with thickness $d \geq 250$ nm after proper annealing were achieved. These Ag(W) films demonstrated high corrosion stability in air at temperatures as high as 350 °C. The σ of thinner Ag(W) films ($d \leq 100$ nm) was about one order of magnitude lower than that for the thicker ones. Vacuum thermal annealing at temperatures $T \geq 150$ °C increased the conductivity of such films. However, the residual conductivity (σ_{res}) of the thin films was significantly lower than that of the thicker layers [10,11]. This phenomenon was studied and possible explanations were proposed [13,14].

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The thin film morphology evolution during the growth was previously explained by coalescence phenomena and percolation mechanism [15,16]. It was shown that in the first stage of the film deposition isolated islands (grains or clusters) appear. Such isolated grains can join by coalescence when a critical size is achieved (Volmer–Weber model) [15,17]. Further deposition of the metal onto the surface results in a formation of elongated torturous network-like structure with conductivity of percolation mechanism. The conductivity of such sophisticated structure may be modeled as an equivalent electrical circuit [18].

In this work we present results of study of the relation between the electrical transport in thin Ag(W) films and its morphology, using Atomic Force Microscopy (AFM) and Tunneling Atomic Force Microscopy (TUNA) technique. We particularly analyzed the evolution of the electrical properties during film growth and after annealing in vacuum.

2. Experimental details

The Ag(W) films were deposited on SiO_2 (20 nm thick) thermal grown on Si wafers. Prior to the deposition the SiO_2 surface was cleaned, slightly etched and activated with a special Pd containing solution as described in Ref. [12]. The electroless deposition was performed from $AgNO_3$ based solution with hydrazine hydrate as a reducing agent. Ammonia and acetic acid were used to complex the metal ions and, at the same time, to support working pH to the range of 11.0–11.3 as an ammonium-acetate buffer. Sodium tungstate (Na_2WO_4) served as a source of tungsten ions. The details of the activation and deposition process can be found in Refs. [9,12].

Ag(W) films, with thickness ranging from 26 to 120 nm, were prepared and analyzed in both as deposited and annealed conditions. Post deposition annealing was performed at 125–300 °C for various time durations, 0.25 to 2 h, in vacuum with residual pressure of 2×10^{-7} Torr. The resistivity of the films was measured by In-Line Four Point Probe with Dual Configuration procedure (Lucas/Signatone™). The film thickness was determined by profilometer Alpha-step 500 (Tencor). The local resistivity of the film was characterized by TUNA method using Conductive Diamond Coated tip (AR10-NCHR10) with radius of curvature in the range between 100 and 200 nm. The TUNA characterization was performed in contact mode, with the feedback loop closed between the output of the position sensitive detector (measuring the deflection of the cantilever) and the *z* (height) axis of the piezo AFM stage, as in regular contact-AFM imaging. Thus the AFM maintained constant tip-to-sample pressure throughout the scan. Due to the high conductivity of the film, the tip bias was set to zero. Under such bias settings the actual (measured) bias between the sample and the tip is ~10 mV. The scan rate was 0.2 Hz, and the tip was internally connected to a *trans*-impedance amplifier with 1 V/nA gain. The TUNA method simultaneously provides both, topography and current images. However, the diamond coated AFM tips used for the current measurements are not optimal for high resolution topography characterization. The topography images obtain in TUNA measurements are merely provided for comparison of current–topography images. Therefore, to obtain high resolution images, Veeco's Dimension 3100 AFM with high aspect ratio silicon tips in tapping mode was used for topography and surface roughness measurements. AFM provided topography data with a resolution of 256×256 pixels and a linear background was subtracted from each scan to compensate a tilt of the sample relative to the scanning plane. For each sample, scans were acquired for scanning area 1.2×1.2 μm^2.

3. Results and discussions

Microscopy studies of the SiO_2 surface coverage by Ag(W) as a function of the metal film thickness have shown that mainly isolated, circular and also several elongated Ag grains initially appear on the substrate (Fig. 1a). The conductivity of this initial deposited material is very small. With further Ag(W)

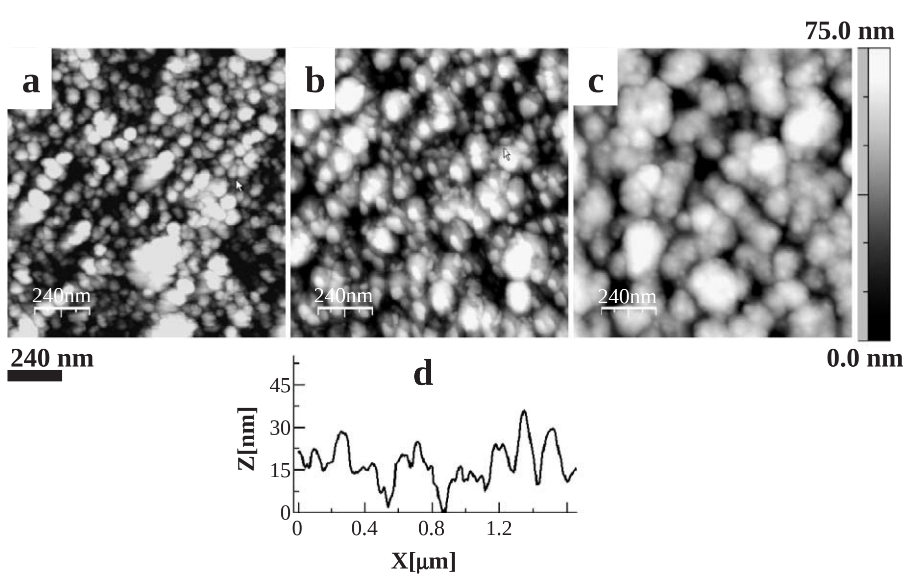

Fig. 1. AFM images of as deposited Ag(W) films: a—30 nm, b—50 nm, c—120 nm and d—the diagonal cross-section of 50 nm Ag(W) film (in Fig. 1b).