Comparative Study of Cu Diffusion in Ru and Ru-C Films for Cu Metallization

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In this paper, the diffusivities of copper in 15 nm thick Ru and Ru–C barrier layers are determined experimentally by using sheet resistance and X-ray diffraction measurements with the Cu/barrier/Si samples. By fitting the dependence of diffusivities on temperature, the activation energy for Cu diffusion in Ru–C film is 1.1 eV, which is substantially higher than that in Ru film (0.54 eV). Microstructural analysis by transmission electron microscopy combined with energy-dispersive X-ray suggests that the higher activation energy for Cu diffusion in Ru–C is associated with the structuring of added carbon atoms on the grain boundaries of the Ru matrix and consequently leading to the superior diffusion barrier performance of the Ru–C film. © 2010 The Electrochemical Society. [DOI: 10.1149/1.3479383] All rights reserved.

Manuscript submitted January 14, 2010; revised manuscript received June 11, 2010. Published September 14, 2010.

Recently, there has been an increasing interest to utilize ruthenium as diffusion barrier and Cu-seed layer in Cu metallization. 1–6 Ru is an air-stable transition metal with a high melting point (2310°C) and nearly half electrical resistivity (7.6 μΩ cm) of Ta (13 μΩ cm). The low solubility of Ru in Cu is an especially favorable attribute for a barrier material, 7 and the Ru film can improve the adhesion of the Cu overlayer. 2,3 Most importantly, the Ru film is an air-stable transition metal with a high melting point (2310°C) and nearly half electrical resistivity (7.6 μΩ cm) of Ta (13 μΩ cm). The low solubility of Ru in Cu is an especially favorable attribute for a barrier material, 7 and the Ru film can improve the adhesion of the Cu overlayer. 2,3 Most importantly, the Ru film allows the direct electroplating of Cu without predepositing a Cu-seed layer. 8 As a consequence, a single Ru layer may be a good candidate of Cu-seed layer as well as a diffusion barrier, which scales down the interconnection dimensions and simplify the fabrication processes.

However, the pure Ru film is not a perfect diffusion barrier and additives are incorporated into Ru to improve its barrier performance because the pure Ru crystalizes easily and forms the columnar structure vertically with respect to Si substrate, either in the as-deposited state or after annealing at low temperatures. 9,10 Therefore, incorporation of other elements, such as N, TiN, and TaN, into Ru films to improve the diffusion barrier property has been investigated in several literatures. 11,12 Unfortunately, the high resistivity of Ru–TaN and Ru–TiN films and instability of N additives in Ru–N film occurred in these barrier layers. However, the 5 nm thick Ru–C film investigated in our previous study 13 has demonstrated an excellent diffusion barrier/Cu-seed property, which would effectively diminish the copper diffusion during prolonged (30 min) annealing up to 700°C.

The activation energy of Cu diffusion in barrier layer is an important parameter for the capability of the diffusion barrier but it cannot be determined straightforwardly. Once the Cu atoms diffuse through the barrier layer to the Si substrate in the Cu/barrier/Si stack structure, the formation of a Cu–Si compound can be detected in X-ray diffraction (XRD) patterns, and the highly resistive Cu–Si greatly increases the whole sample resistance. 14 Therefore, the sheet resistance (SR) variation and XRD patterns of the Cu/barrier/Si samples are the possible methods to obtain the onset of the Cu–Si formation as a function of annealing temperatures, which serves as an index for the diffusion of Cu through the whole barrier layer. Subsequently, the diffusivity and activation energy of Cu diffusion in the barrier can be extracted. The activation energy for Cu diffusion in various kinds of diffusion barriers, such as TaN and TiN, has been reported. 15–17 However, the activation energy of the Cu diffusion in Ru and Ru-based thin films has not been investigated in any literature.

In this study, 15 nm thick Ru and Ru–C barrier films are applied as the diffusion barrier layer for Cu metallization and the activation energies of Cu diffusion in the barriers are carefully measured from the experimental results of SR variation and XRD patterns of Cu/barrier/Si samples as a function of annealing temperatures. Also, the location of the added carbon atoms in the Ru–C film and the correlation between the barrier performance and microstructure of the Ru–C layer are also discussed.

Experimental

P-type silicon (100) wafers with resistivity of 1–10 Ω cm were used as the starting substrates. The substrates were cleaned by a standard RCA method. Before deposition, the substrates were dipped into diluted HF to remove the native oxide and then the substrates were loaded into the vacuum chamber immediately. 15 nm Ru–C films were deposited on p-Si(100) substrates by cosputtering with Ru (99.95% purity) and C (99.999% purity) targets at dc power of 100 W and radio-frequency (13.56 MHz) power of 400 W, respectively. The sputtering atmosphere for the Ru–C films was pure Ar with a flow rate of 30 sccm. The resulting composition is 76% Ru, 19% carbon, and 5% oxygen, as determined by Rutherford backscattering spectrometry. 15 For comparison, pure Ru films with thickness of 15 nm were deposited on Si substrates under the same deposition condition. Cu films of 50 nm thick were deposited on barrier layers by sputtering a Cu (99.999% purity) target at a dc power of 100 W and a negative substrate dc bias of 100 V. To determine the diffusivity and activation energy of Cu diffusion in the barrier layers, the Cu/barrier/Si stacks were annealed in a vacuum furnace under a pressure of 2 × 10−5 Torr (together with Ti foils to reduce the residual oxygen) at temperatures ranging between 500 and 900°C for different annealing times.

The SR of Cu/barrier/Si samples was measured with a four-point probe as a function of annealing time at different annealing temperatures. The characteristic phases of all samples were also identified by an X-ray diffractometer (Rigaku MultiFlex) using Cu Kα radiation (λ = 0.1542 nm). The microstructure of selected Cu/Ru/Si samples and the Ru–C barrier layer were investigated by a high resolution transmission electron microscope (HRTEM, FEI E.O Tecnai F20 G2 field emission) operating at 200 kV. An energy-dispersive X-ray spectrometer (EDX), combined with transmission electron microscopy (TEM) was used to determine the elemental compositions of local regions of the Ru–C barrier on a cross-sectional TEM micrograph by using the smallest electron beam spot size of 2 nm.

Results and Discussion

In this work, the Cu overlayer is treated as a source of Cu atoms of constant surface concentration to model the diffusion of Cu into the underlayers in the Cu/barrier/Si system. For constant surface concentration diffusion, the concentration profile of atoms can be expressed by Eq. 1.15