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The effects of nitrogen incorporation on the properties of atomic layer deposited Ru thin films as a direct-plateable diffusion barrier for Cu interconnect

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ABSTRACT

N-incorporated Ru films were deposited by atomic layer deposition (ALD) at a deposition temperature of 270 °C using 1-isopropyl-4-methylbenzene-cyclohexa-1,3-dienyl ruthenium and N_2/H_2 mixture plasma as the precursor and reactant, respectively. The N content in the ALD-Ru films was controlled by changing the gas ratio [N_2 versus the total gas ($N_2 + H_2$) flow rates] in the reactant from 0.82 to 1. Secondary ion mass spectrometry depth profiling revealed an increase in N content in the film with increasing gas ratio. The amount of N in the ALD-Ru films had a considerable effect on the film properties, such as resistivity, crystallinity and microstructure. Although the resistivity of the pure ALD-Ru film was ~19 μΩ cm, the N-incorporated ALD-Ru films deposited with a gas ratio of 0.86 (N/Ru: ~0.38) showed a resistivity of ~340 μΩ cm, which increased continuously with increasing gas ratio. X-ray and electron diffraction revealed degradation in film crystallinity and decrease in grain size with increasing N incorporation into ALD-Ru films. Transmission electron microscopy showed that N-incorporated ALD-Ru films formed nanocrystalline and non-columnar grain structures. This is in contrast to that observed in the pure ALD-Ru film, which had a polycrystalline columnar grain structure. The growth rate of a representative N-incorporated Ru film deposited with a gas ratio of 0.86 showed a linear dependency on the number of ALD cycles; growth rate of 0.051 nm/cycle at short incubation cycles of ~3. The step coverage was approximately 98% over the trench structure (aspect ratio: 4.5) with a top opening width of 25 nm. The direct plating of Cu on an optimized N-incorporated ALD-Ru film (5 nm in thickness) was possible. The structure of Cu (80 nm)/N-incorporated ALD-Ru (8 nm)/Si was found to be stable without the formation of copper silicide after annealing at 600 °C for 30 min.

1. Introduction

Ruthenium (Ru) is a noble metal with good thermal and chemical stability, low resistivity (7.1 μΩ cm for bulk), and a large work function (4.7 eV). These excellent physical, chemical and electrical properties have prompted studies of Ru thin films for a range of applications in semiconductor device fabrication, such as a gate for metal-oxide-semiconductor transistor [1,2] and electrode for a capacitor in dynamic random access memory [3,4]. Ru adheres well to copper (Cu) [5,6] because of its low solid solubility in Cu [7], and promotes a better Cu (111) texture than Ta [8], making Ru the most promising material for back end of line Cu-wiring as a seed layer or adhesion layer, and even as a Cu direct-plateable diffusion barrier. Here, a Cu direct-plateable diffusion barrier should function both as a diffusion barrier against Cu and a seed layer for the electroplating (EP) of Cu [9–12]. The application of a Cu direct-plateable diffusion barrier for Cu metallization can secure the space needed for Cu to be plated and mitigate the drastic increase in the resistivity of Cu wiring due to the size effect [13,14] with device scaling-down. A suitable process is needed to guarantee excellent step coverage of Cu direct-plateable diffusion barriers as the device size is scaled down. In this respect, atomic layer deposition (ALD) is one of the most promising techniques for growing thin films because of its simplicity, reproducibility, atomic-scale control of the film thickness and composition, and the high conformality of the resulting films. These unique advantages of ALD are mainly the self-limited growth mechanism, and the readers can refer to excellent recent reviews [15–17].

Ru has been evaluated as a Cu direct-plateable diffusion barrier but previous studies reported that Ru itself is unsuitable as a diffusion

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barrier for Cu metallization, despite Cu electroplating being successful [5,8,18,19]. A 20 nm thick sputter-deposited Ru film was reported to prevent Cu diffusion between Cu and Si at temperatures up to 450 °C [5], whereas a similar Ru film with a thickness of 5 nm lost its barrier properties at only 300 °C [18]. It was also reported that a 15 nm thick sputter-deposited Ru film prevented Cu diffusion between Cu and Si until 400 °C annealing [19]. Therefore, the diffusion barrier performance of Ru film needs to be improved for it to be integrated as a Cu direct-plateable diffusion barrier. The poor diffusion barrier performance of Ru was attributed mainly to its microstructure with polycrystalline columnar grains that provides a fast diffusion pathway for Cu [19]. To improve the poor diffusion barrier performance of Ru against Cu, several efforts have been made to modify the microstructure of Ru to an amorphous or nanocrystalline structure [20–23]. The basic idea is to incorporate materials into Ru during deposition to produce Ru-based ternary thin films by ALD, such as Ru-TaN [20], Ru-WCN [21], RuSiN [22] and RuAlO [23].

In a previous study, N-incorporated ALD-Ru films and pure ALD-Ru films were deposited by controlling the ratio of N_2:total gas ($N_2 + H_2$) flow rates in the plasma as a reactant [24]. Considering that nitrogen incorporation in sputter-deposited Ru results in a change in its microstructure from columnar to nanocrystalline [25], previous studies suggest that an N-incorporated ALD-Ru film is a potential Cu direct-plateable diffusion barrier. The present study examined N-incorporated ALD-Ru films further. A series of N-incorporated ALD Ru films were prepared with different gas ratios and their properties, such as resistivity, composition and microstructure, were examined according to the deposition conditions. Finally, N-incorporated ALD-Ru film was evaluated as a Cu direct-plateable diffusion barrier. In particular, the step coverage on a nano-scaled trench structure was checked, its thermal stability was evaluated, and direct Cu plating was performed on the N-incorporated ALD-Ru film.

2. Experiments

N-incorporated ALD-Ru films were deposited on a thermally grown SiO_2-covered Si wafer using a showerhead-type ALD reactor with (η6-1-isopropyl-4-methylbenzene)(η4-cyclohexa-1,3-diene)ruthenium (0), IMBCHDRu as a precursor. The deposition temperature and chamber pressure were 270 °C and 133.3 Pa, respectively. The Ru precursor was vaporized in a bubbler at 100 °C and carried into the process chamber with Ar gas at 50 standard cubic centimeters per minute (sccm). As a reactant, a mixture of N_2 and H_2 gas was flowed into the chamber with a radio frequency (RF) plasma power of 100 W. The gas ratio of N_2 versus total gas ($N_2 + H_2$) flow rates ($f_{N2/N2+H2}$) varied from 0.82 to 1.00 with the amount of total gas flow rates maintained as 50 sccm. Between the precursor pulsing and reactant pulsing, a purging process was performed using 200 sccm of Ar gas. Based upon previous studies on a pure ALD-Ru process using the same precursor and reactant [24], N-incorporated ALD-Ru films were typically grown with a Ru precursor pulse time of 7 s and a plasma pulsing time of 12 s, which guarantees self-limited film growth.

The properties of the N-incorporated ALD-Ru films deposited with different gas ratios were analyzed using a range of tools. The film thickness was determined from X-ray reflectance (XRR, PANanalytical X′-pert PRO MRD with Cu-Kα radiation at 1.5 kW). The resistivity was determined by combining the sheet resistance of the films measured using a four-point probe with their thicknesses. The film compositions were characterized by Rutherford backscattering spectrometry (RBS) and secondary ion mass spectrometry (SIMS, CAMECA IMS-6f installed in Korea Basic Science Institute) depth profiling, whose results were calibrated by nitrogen resonance RBS. The nitrogen resonance RBS techniques (incident energy of He^{++}: 3.695 MeV) was used to detect N in the film. First, the composition of N-incorporated ALD-Ru film deposited with a gas ratio of 0.88 was determined using nitrogen resonance RBS. In addition, the same sample was analyzed by SIMS and the sensitivity factors for the quantification of each element in the film were determined. For further SIMS analysis, the sensitivity factors were used to determine the compositions of the N-incorporated ALD-Ru films deposited with various gas ratios. X-ray diffraction (XRD) was performed for phase and crystallinity identification. Plan-view transmission electron microscopy (TEM, Tecnai F20 equipped with 200 kV accelerating voltage and field emission gun) and cross-sectional-view TEM (XTEM) were used to examine the microstructure of the films depending on the deposition conditions.

The properties of N-incorporated ALD-Ru films deposited with a gas ratio of 0.86 were evaluated in view of the integrations as a Cu direct-plateable diffusion barrier. In particular, the step coverage of the N-incorporated ALD-Ru film without a diffusion barrier was investigated at a trench structure (top opening width of 25 nm and AR of ~4.5). The thermal stability of N-incorporated ALD-Ru film was next evaluated. To examine the thermal stability, N-incorporated ALD-Ru films deposited with a gas ratio of 0.86 were annealed in a high vacuum ($<2.67 \times 10^{-4}$ Pa) for 10 min at temperatures ranging from 400 to 600 °C at 100 °C intervals. The thermal stability was characterized according to the composition, phase and crystallinity after annealing. Cu was then electrodeposited on a 5-nm thick N-incorporated ALD-Ru film to confirm the feasibility of the film as a seed layer for Cu electroplating. The Cu plating bath consisted of 0.05 M $CuSO_4 \times 5H_2O$, 0.05 M $(NH_4)_2HC_6H_5O_7$, and NH_4OH for pH adjustment. The pH of the bath was 7.0. The Cu films were grown directly on the N-incorporated ALD-Ru film by applying a constant cathodic potential of − 1.0 V versus a saturated calomel electrode (SCE). Potentiostatic deposition was carried out using a potentiostat (IviumStat, Ivium Technologies Inc.). Finally, the diffusion barrier performance of the N-incorporated ALD-Ru film between Cu and Si was evaluated. To evaluate the barrier performance of the N-incorporated ALD-Ru film, 80-nm-thick Cu films were deposited onto 8-nm-thick N-incorporated ALD-Ru-covered Si wafers by sputtering. These Cu/N-incorporated ALD-Ru/Si samples were then annealed in a high vacuum ($<2.67 \times 10^{-4}$ Pa) for 30 min at temperatures ranging from 500 to 600 °C at an interval of 50 °C. The barrier performance after annealing was evaluated by sheet resistance measurements and XRD.

3. Results and discussion

3.1. Effects of N incorporation on the properties of the ALD-Ru films

Fig. 1 shows the film thickness and resistivity as a function of the gas ratio in the reactant. The total number of ALD cycles was 400. Generally, both properties increased with increasing gas ratio. The resistivity increased from 70 to 340 μΩ cm with an increasing gas ratio from 0.82 to

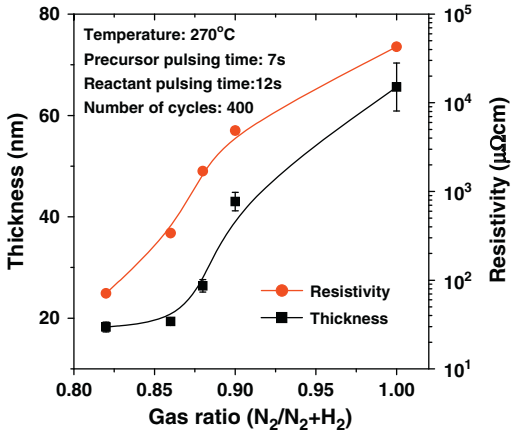

Fig. 1. Thickness and resistivity of the N incorporated ALD-Ru films deposited as a function of the gas ratio (N_2 versus total gas flow rates: $f_{N2/N2+H2}$).