Characteristics of Pulse Plasma Atomic Layer Deposited WC_xN_y Diffusion Barrier For Copper Interconnect

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As the semiconductor device dimension has been shrinking down continuously, interconnection materials low resistivity and high resistance to with electromigration is one of key issues. Therefore, copper interconnection has been intensively studied for the multilevel interconnection in ultra large-scale integrated devices. However, problems such as high diffusion coefficient of copper in both silicon and silicon dioxide and deep acceptor level traps in the forbidden gap have to be solved prior to practical application of Cu interconnection. Therefore, metal-nitride materials such as TaN, TaSiN, and W-N have been suggested to prevent the Cu diffusion instead of TiN [1-3]. TiN has been popularly used as a diffusion barrier but it has the dominant diffusion path through the columnar TiN grain boundaries so that the TiN can not be adequate as a diffusion barrier for the Cu interconnect [4-5]. Among the new metal-nitrides, WCxNy diffusion barrier has received less attention for the future multilevel interconnects because there is few result on the characteristics of WC_xN_y diffusion barrier. For the Cu interconnection technology, very thin and thermally stable diffusion barrier film is required as well as low resistivity for achieving the Cu interconnection. Therefore, first of all, it is an essential issue how to prepare very thin diffusion barrier and this very thin diffusion barrier must prevent the Cu diffusion and to maintain amorphous or nanocrystalline phase to suppress the grain boundary diffusion path during the post-annealing processes at 600 $^{\circ}$ C. On this viewpoint, we need to deposit the WC_xN_y thin films with atomic layer deposition (ALD) method. However, it is nearly impossible to obtain homogenous WC_xN_y thin film with ALD method because the ternary source gases are still in question excepting WF₆, CH₄ and NH₃. Furthermore, these gases do not easily adsorb on the inter-dielectric layer, which will be a dominant difficulty for the ALD method. Therefore, there are some results to deposit the W-N films with ALD method by using bis(tert-butylimido)bis(dimethylamido)tungsten,

 $({}^{t}BuN)_{2}(Me_{2}N)_{2}W$ gas, resulting in very high resistivity or to modify the SiO₂ surface with SiCl₄ gas [6-7]. In this work, we have developed a new method to apply very short pulse plasma for the exposure time of source gases, introducing the reactive source gases instead of the normal gases into the ALD reactor to enhance the adsorption of source gases on the SiO₂.

We prepared p-type Si(100) wafers and grown 200 nm thick SiO₂ layer by thermal oxidation method. On this SiO₂ layer we have deposited the WC_xN_y thin films with pulse plasma enhanced atomic layer deposition (PPALD) method by using WF₆, CH₄ and NH₃ gases. WF₆ gas was introduced for 0.2 s and then purge process was carried on with N₂ purging gas. After that, CH₄ gas was introduced for 0.3 s and evacuated with N₂ purge process and next WF₆ gas was exposed and carried out purge process. Finally NH₃ gas was also introduced for 0.3 s and purged with N₂ gas. This was a cycle that was sequentially repeated during the ALD process. Pulse plasma was applied for the both exposure times where the CH₄ and the NH₃ gases were introduced into the reactor,

separately. The pulse plasma power was ~8 kV of peakto-peak voltage. The substrate temperature was 250 to 400 °C. Stoichiometric ratio of WC_xN_y was characterized by Rutherford back scattering (RBS) and Auger electron spectroscopy (AES). The interface between WC_xN_y film and Si substrate was observed by high-resolution transmission electron microscopy (HRTEM). Fig. 1 shows that the N and C concentration is uniformly distributed in the WCxNy film during the PPALD processes and fluorine impurities are below than the detection limit of AES because the pulse plasma removes the fluorine atoms from WF_6 at the adsorption stage. It is well known that these F atoms remained in the WC_xN_y film lead to high resistivity and it will deteriorate the performance of diffusion barrier against the Cu. In order to investigate the properties of PPALD grown WC_xN_v diffusion barrier, 200 nm thick Cu film was deposited on the WC_xN_y/SiO_2 . The $Cu/WC_xN_y/SiO_2$ samples were annealed at 500~700 °C for 30 min in N2 ambient. After the annealing processes, the samples were measured with RBS, AES and HR-TEM to determine whether the Cu diffusion was occurred or not through the WC_xN_y diffusion barrier. Experimental results show that the WC_xN_y films successfully prevents the Cu diffusion even after the annealing at 700 °C for 30 min.

In this work, we will discuss the ALD mechanism for the WC_xN_y in detail and effects of C and N concentrations on the film resistivity thoroughly.



Fig. 1. AES depth profile of W-C-N film deposited on SiO_2 at 350 $^{\circ}\text{C}$ for 100 cycles by PPALD method

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