Kinetics and transport of Cu and CuCl in Cu film deposition by metal chloride reduction plasma CVD

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1. Introduction

Metal chloride reduction chemical vapor deposition (MCRCVD) is a new method for forming barrier and seed layers inside trenches and holes on insulation layers of ultralarge-scale integrated circuits. In this method, Cu thin films are formed by the following three steps. The first step is chemical etching of a Cu target immersed in a Cl₂/He mixture plasma to produce CuCl. The second step is the transport of CuCl toward the substrate. In the final step, CuCl is reduced by Cl radicals to leave pure Cu films on the substrate. This method has advantages in the simple source gas and a low substrate temperature, in comparison with metal organic compound chemical vapor deposition. The key points of this process technology are the production and the transport of CuCl from the target to the substrate. In the transport, CuCl radicals are dissociated into Cu by electron impact, which should be avoided as much as possible to obtain CVD-mode deposition using CuCl as the precursor. In this work, we investigated the kinetics and transport of CuCl and Cu in Cl₂/He mixture plasmas by visualizing their density distributions using laser-induced fluorescence (LIF) imaging spectroscopy.

2. Results and discussion

Figure 1 shows the temporal variation of the Cu atom density after the initiation of the discharge, together with the axial distributions at four delay times. The discharge power was 500 W and the gas pressure was 110 mTorr with a Cl₂ percentage of 30%. The temporal variations of the Cu densities at 3 mm above the target and at 5 mm above the substrate are plotted. The locations of the target and the substrate are 37 and 69 mm, respectively, in the axial distance. We observed a burst-like increase in the Cu density immediately after the initiation of the discharge. This may be originated from the burst-like desorption of CuCl from the target since the increase in the Cu density was more remarkable at the position near the target. On the other hand, at 900 s after the initiation of the discharge, we observed another burst-like increase in the Cu atom density. The second burst-like increase was more remarkable above the substrate, which suggests that the second burst-like increase in the Cu density is caused by burst-like desorption of CuCl from the substrate surface. The aforementioned production and the transport processes are also understood from the axial distribution of the Cu density. During the first burst-like increase (80 s), the gradient of the Cu atom density had the direction from the target to the substrate, indicating the diffusion transport from the target to the substrate. On the other hand, the gradient of the Cu atom density during the second burst-like increase (950 s) in the Cu density was opposite, indicating the diffusion transport from the substrate toward the upstream region. The reaction kinetics and the transport processes are understood more clearly by considering the CuCl radical density, which will be shown at the symposium.