Low-temperature and Low-damage Metal CVD with High-density Cl_2 Plasma

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1. Introduction

The Metal Chloride Reduction Chemical Vapor Deposition (MCR-CVD) is a new film deposition method based on the reaction discovered independently by Mitsubishi Heavy Industries, Ltd. (MHI)(1).

The film deposition applies high-density plasma solely using chlorine gas, contributing to reduction in material cost and ensuring the process at a low temperature. Further, since chlorine radical reaction involving no electric charge is mainly used, the damage to the substrate surface can be minimized. Besides, since the etching reaction and the film deposition reaction coexist in the system, a wide range of deposition control can be made from the so-called "bottom-up" deposition(2) (where the deposition takes place from the bottom for the fine pattern) to the conformal film deposition.

These features are considered indispensable to the manufacturing process of future electronic devices such as the Ultra Large Scale Integrated circuit (ULSI) and Flat Panel Display (FPD). This paper throws light in the applicability of the deposition method taking titanium, iridium and tantalum nitride as examples.

2. Apparatus

The MCR-CVD method introduces chlorine gas into the space between the bulk metal and the substrate, and applies radiofrequency power to the induction coil surrounding the space to generate chlorine plasma. The large quantity of chlorine radicals contained in the plasma carries out etching of the bulk metal to form metal chloride, and eventually deposits the metal film by reducing the metal chloride adsorbed on the substrate surface.

The photograph above shows the appearance of a MCR-CVD apparatus for 8-inch wafer currently under development. The apparatus composed of 1 load lock + 1 chamber, while the chamber comprises a loop antenna for generating plasma with an exchangeable metal target located right under the antenna.

3. Example of film deposition

3.1 Titanium film deposition(3)

Titanium is a material frequently used in semiconductor devices, and the titanium film is formed recently by using sputtering method or CVD method especially as contact layer of interconnects, barrier layer and etching stop layer. With the devices getting more and more miniaturized, however, the damage to the surface by charged particles in the case of sputtering method and the excessively high temperature at the time of film deposition (>400°C) and a high-concentration residual chloride (>5%) in the film in the case of normal CVD method are becoming problems.

Fig. 1 shows a 50 nm thick film deposited at the rate of 3 nm/min at substrate temperature 300°C on a hole pattern (diameter: 0.5 μ m, depth 1.2 μ m) using MCR-CVD method. The film is deposited conformally over the entire pattern, with the chlorine concentration in the film found to be 2% and the specific resistance 1.0 mΩ•cm (bulk specific resistance: 42 μΩ•cm). The failure in substantial drop of specific resistance is seemingly attributed to the intake of residual water content in the atmosphere. However, the titanium film with chlorine concentration lower than the film deposited by conventional method could be obtained by using MCR-CVD method.

3.2 Iridium film deposition(4)

Iridium is one of the capacitor electrodes in Ferro-electric Random Access Memory (FeRAM) currently being developed as a next generation non-volatile memory. Similar to the aforesaid metal titanium, its film has so far been formed using sputtering method or through MOCVD (Metal Organic Chemical Vapor Deposition), but was not sufficiently effective in view of coverage and adhesiveness and was excessively high in terms of material cost.

Fig. 2 shows a 50 nm thick film deposited at the rate of 4.2 nm/min at substrate temperature 300°C on a hole pattern (diameter: 0.5 μ m, depth: 1.2 μ m) using MCR-CVD. Here, the existence of chloride on the initial boundary surface of the film causes silicon substrate erosion to take place solely to the deposited iridium film. Hence, a tantalum protection film was formed at the bottom of the hole using MCR-CVD before depositing the iridium film. This led to formation of a film with coverage as excellent as that of titanium together with the chloride concentration 1% in the film and the specific resistance 1.27mΩ•cm (bulk specific resistance: 4.7 μΩ•cm). In this case also, the inclusion of residual moisture in the film seems to have caused failure in substantial drop of specific resistance, but iridium film with more adhesiveness and coverage than the film formed by conventional method could be obtained.

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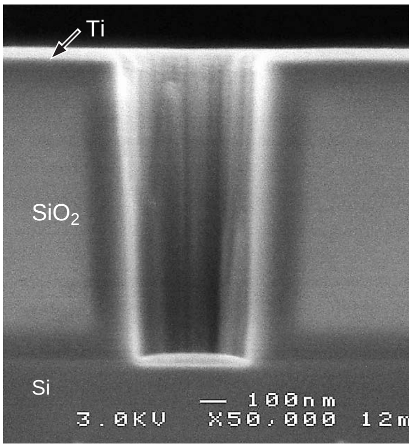

Fig. 1 SEM photograph of titanium film deposition on a hole pattern
The film is conformally deposited on the hole with diameter: 0.5 μm and depth: 1.2 μm.

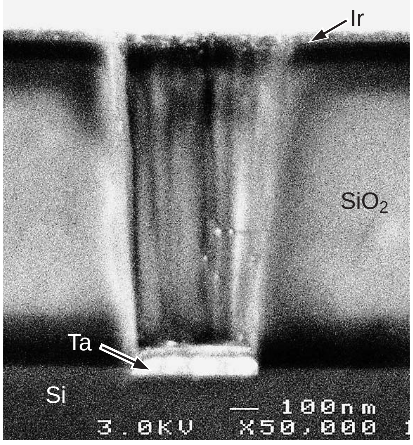

Fig. 2 SEM photograph of iridium film deposition on a hole pattern
The film is conformally deposited on the hole with diameter: 0.5 μm and depth: 1.2 μm.

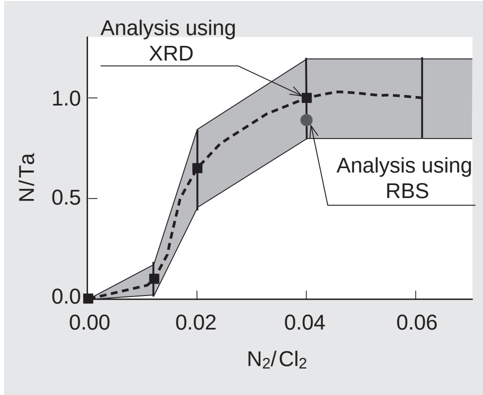

Fig. 3 Dependence of N/Ta ratio in tantalum nitride film on nitrogen flow rate
Shows an increase in N/Ta as the nitrogen flow rate increases. Analysis was made using two methods XRD and RBS and the result being almost same in both cases.

3.3 Tantalum nitride film deposition(5)

Tantalum nitride is greatly expected as a barrier film for Cu interconnects of ULSI because of its outstanding diffusion-stopping capacity, or as a gate metal electrode film for ULSI because the work function can be controlled by changing the nitrogen-tantalum composition (N/Ta ratio). In the former case the sputtering method or the Atomic Layer Deposition (ALD) can be applied to some extent, but in the case of the latter, there was no substantially applicable film deposition method because of the low controllability of N/Ta and excessively large damage to the extremely thin gate insulating film (<2 nm). MHI, therefore, applied MCR-CVD method as an experiment based on the concept that metal nitride or metal oxide film deposition was possible by slightly mixing nitrogen or oxygen.

Fig. 3 shows the change in N/Ta ratio contained in the film when the added nitrogen quantity against the introduced chlorine quantity is changed when a 60 nm thick film is deposited at the rate of 20 nm/min. Here, the composition is evaluated by using X-ray Diffractmeter (XRD) and Rutherford Backscattering Spectroscopy (RBS). It was confirmed through the experiment that the work function could be controlled since the N/Ta ratio showed a drastic increase by adding a small quantity of nitrogen. In the experiment, the under layer coat of 2 nm thick silicon oxide film was confirmed to have no damage through transmission electron microscope.

4. Conclusions

The paper describes the features and wide application of the newly developed metal deposition method, MCR-CVD, taking titanium, iridium and tantalum as examples. MHI is currently engaged in building up a close and cooperative system with customers from the stage of research and development, keeping in mind the aforesaid advantages of MCR-CVD. Under the basic policy of prompt response to customer's needs through simulation, etc., we are determined to making way into the market of semiconductor manufacturing devices.

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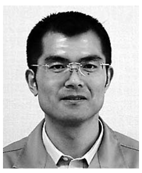
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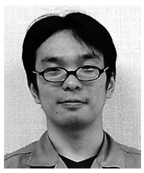
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