論 文 の 内 容 の 要 旨

論文題目　Quantitative evaluation of barrier properties of ultra-thin PVD-Co(W) diffusion barrier layer in Cu interconnects by developing a new method

（新規手法開発によるCu多層配線用極薄PVD-Co(W)膜の拡散バリア性の定量的評価）

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This dissertation focused on the development of a new method for the quantitative evaluation of barrier properties for continuously miniaturized Cu interconnect in ultra-large-scale integration (ULSI) devices. Quantitative evaluation of barrier properties is essential to make an effective barrier layer in Cu interconnects. This will help us understand the diffusion phenomenon of future Cu interconnects.

In chapter 1, I summarized the issues arising from the miniaturized Cu interconnects so far and discussed the solution. Cu generally diffuses into Si in the semiconductor manufacturing process, creating an active deep level. Therefore, the development of effective diffusion barriers for Cu interconnects is the most important issue. Cu interconnects generally have Cu/liner/barrier/low-k structures. The latest ULSI device needs to have a thinner liner/barrier layer in order to maintain the cross-sectional area of Cu. However, there are some difficulties when technology node is extremely miniaturized; (1) resistance-capacitive (RC) signal delay, (2) electro-migration (EM) and stress-induced voiding (SIV). Subsequently, specific requirements to solve the issues were summarized from the viewpoints of material, structural, and manufacturing. The liner/barrier layer should not to react chemically with Cu and should not to dissolve Cu. In order to satisfy these requirements, I proposed amorphous Co(W) single layer made by physical vapor deposition (PVD).

In addition, the methods of evaluating barrier properties for Cu diffusion have been systematically organized; (1) qualitative, (2) semi-quantitative, and (3) qualitative evaluation. (1) The method in which any numerical discussion cannot be made from the measurement results is called a qualitative evaluation method. The qualitative evaluation method only evaluates whether the barrier layer prevents diffusion or whether the barrier layer has lost its barrier properties due to diffusion. (2) The semi-quantitative evaluation method can numerically evaluate the change in barrier properties to some extent. If the results of changes in measurement conditions can be compared numerically, at least the superiority and inferiority of the barrier properties will be masked. (3) A method capable of directly measuring the quantity of diffused Cu is called a quantitative evaluation method. Since the quantity of diffused Cu is directly used, the barrier properties can be evaluated most accurately. Finally, the importance of quantitative evaluation of Cu diffusion represented by diffusion coefficient (*D*) was explained.

In Chapter 2, the quantitative evaluation of the barrier properties of 20-nm-thick PVD-Co(W) for Cu was covered. Its principles and experimental methods was also explained. Samples of the stacked structure [100-nm-thick Cu / 20-nm-thick PVD-Co(W) / 100-nm-thick SiO_2 / Si wafer] were annealed by rapid thermal anneal (RTA). After annealing, the concentration profile of Cu diffused into PVD-Co(W) was obtained by X-ray photoelectron spectroscopy (XPS). At this time, for the first time, the back-side depth profile method was applied. The experimental concentration profile of Cu obtained by XPS was then fitted to a theoretical profile based on Fick's second law and *D* was determined. Changes in barrier properties according to W concentration changes were investigated using samples of six different Co and W composition. For the Arrhenius plot of PVD-Co(W) film with six different W concentrations, the logarithm of *D* varied linearly against reciprocal of temperature in the range of 500 to 700ºC. This means that the diffusion mechanism of Cu in Co(W) was unchanged in this temperature range. *D* at 500°C was compared with ALD-Co(W) with W 20 at. % and PVD-TaN, because it was the closest to the temperature used in the back end of line (BEOL) manufacturing. Of the W concentrations tested, PVD-Co(W) with W 43 at. % showed the lowest *D*, and thus expecting better Cu diffusion barrier properties than PVD-Ta/TaN and ALD-Co(W). Therefore, PVD-Co(W) with W 43 at. % was considered to be optimal for BEOL manufacturing. Crystallinity and resistivity results were also measured to find the optimal composition of PVD-Co(W) single layer. From the results of crystallinity, the cause of the excellent barrier properties of PVD-Co(W) was predicted. Thanks to the amorphous-like structure containing trace quantity of Co crystals, fast diffusion paths such as grain boundaries did not occur, as a result, excellent barrier properties seem to be maintained. The significance of this chapter is that it is a starting point for quantitative evaluation of the barrier properties of PVD-Co(W) single layer. If quantitative evaluation is successfully introduced, it will be possible to predict what will happen in the initial stage of thin film growth. The adhesion was also additionally discussed. To evaluate adhesion, the contact angle of the cross-sectional image of SEM were used. From the results, the dependence of the adhesion on the change of the W concentration was investigated. The excellent adhesion of PVD-Co(W) was confirmed through comparison with the results of ALD-Co(W).

Chapter 3 deals with the process of establishing a quantitative evaluation method of barrier properties for thinned PVD-Co(W). A quantitative evaluation of the barrier properties using the depth profile method has already been completed in previous chapter. However, the depth profile method is difficult to apply to ultra-thin films such as 1 or 2 nm. This is because, in the depth profile method, a barrier layer having a certain thickness is essential for the concentration profile of diffused Cu. Therefore, it is essential to develop a method capable of quantitative evaluation of ultra-thin films. First of all, quantitative evaluation using atomic probe tomography (APT) was attempted. Then, considering the reason why the APT measurement failed, I could obtain the experimental results using inductively coupled plasma-optical emission spectrometry (ICP-OES). For this, I developed the modified time-lag method to measure the trace quantity of Cu passing through the Co(W) barrier. The sample was [Cu/Co(W)/sputtered SiO_2/Ti/Co(W)/SiO_2/Si substrate]. The whole procedure of the modified time-lag method after annealing was as follows. (1) The Cu and Co(W) were etched by $FeCl_3$ solution. (2) The diffused Cu in the SiO_2/Ti/Co(W) structure was dissolved with 1HF (5%) + 1HNO_3 (5%) mixed solution. (3) The Cu concentration [ppb] in the mixed solution was measured using ICP-OES. (4) It was converted Cu concentration [ppb] into the quantity of Cu atoms per unit area passing through the barrier layer [mol/cm^2]. By repeating these procedures at various annealing temperatures, D was obtained. I can obtain Q-t plot from the x-axis represents annealing time (t) and the y-axis represents the number of diffused Cu moles per unit area (Q). The slope in Q-t plot denotes a flux of the substance passing through the barrier. The x-intercept in Q-t plot is called "time-lag". According to the analytical solution of the diffusion equation, relations between D and x-intercept or slope are given by,

$$\text{(x intercept, i.e. time-lag)} = \frac{L^2}{6D} \qquad (1),$$

$$\text{(slope, i.e. flux)} = \frac{DC_0}{L} \qquad (2),$$

where C_0 is the concentration of diffused substance at the upstream interface of the barrier, and L is a thickness of the barrier. D is, therefore, obtained from the time-lag using equation (1), since L is known in general prior to the measurement. D is also obtained from the slope using equation (2), since C_0 is the experimental condition. To prove the validity of the modified time-lag method, two D values obtained using the x-intercept and slope from the Q-t plot were compared. It was confirmed that the results obtained from the modified time-lag method are valid. Through comparison with the result of 20-nm-thick PVD-Co(W), it was possible to predict the change in barrier properties according to the change in the thickness of the thin film. The barrier properties of PVD-Co(W) were quantitatively evaluated using the modified time-lag method, and the reliability of the results was also secured. Using this method, D can be obtained theoretically no matter how thin the barrier layer is. It is meaningful that it is possible to quantitatively evaluate the barrier properties even in miniaturized Cu interconnects.

Chapter 4 mainly deals with the quantitative evaluation of the barrier properties of thinned PVD-Co(W). The modified time-lag method was used to discuss the thickness dependence and temperature dependence of the barrier properties of PVD-Co(W) layer. The thickness dependence of barrier properties is important because the starting point for miniaturization of Cu interconnects is the thickness dependence of the barrier layer. It would be desirable if the barrier properties are improved as the thickness of the barrier layer became thinner. On the contrary, if the barrier properties decrease as the thickness of the barrier layer becomes thinner, the cause should be investigated. However, it is not known whether or not the barrier properties change depending on the thickness of the barrier layer.

The barrier properties were quantitatively evaluated by experimentally estimating the *D* of Cu for 8, 10, 12-nm-thick PVD-Co(W) layer in the 780, 830, and 855°C. *D* increases as the annealing temperature increases. At the same annealing temperature, *D* tends to decrease slightly as the PVD-Co(W) barrier becomes thinner. The activation energy (E_a) for Cu diffusion in the 780, 830, and 855°C was obtained to explain the diffusion behavior from the nanostructure point of view. From the results, it was confirmed that the thinned PVD-Co(W) has excellent barrier properties. When the thickness of PVD-Co(W) layer changes, the change in *D* is important for understanding the barrier properties. The reason why the barrier properties of the thinned barrier are further improved is that the thinner the barrier, the stronger the amorphous structure of the barrier. Basically, as the thin film becomes thinner, the probability of nucleation required for crystallization decreases. Therefore, the thinner the thin film, the more improved the amorphous state could exist. In addition, it is also an important data to understand the diffusion phenomenon occurring in the initial stage of thin film growth.

In addition to the barrier properties of thinned PVD-Co(W) thin films, I further discussed crystallinity. From the result of XRD, it was confirmed that crystallization of Co and W did not occur. The reason for the superiority of the barrier properties was proved by combining the crystallinity results and the barrier properties results.

In Chapter 5, I organized the contents of achievements through my research. (1) The quantitative barrier properties of PVD-Co(W) were evaluated using the back-side depth profile method. (2) For the first time, modified time-lag method for Cu interconnects has established to quantitatively measure the barrier properties of the thinned barrier layer. (3) The modified time-lag method was used to find out whether the barrier properties change according to the thickness of the barrier layer. Based on the research results, several proposals were made for the diffusion field of Cu interconnects; (1) Optimal thin film conditions for using PVD-Co(W) as a single liner/barrier layer, (2) A single layer incorporating barrier properties and adhesion properties, (3) The need for a metal liner/barrier layer, (4) Application to dual damascene trench structure, and (5) The possibility of PVD in the fabrication of extremely thin barrier layers such as 1 nm. Finally, the remaining tasks were arranged; (1) Possibility for quantitative evaluation of barrier properties even for 1 nm barrier layers, (2) Investigating how the *D* and E_a vary according to the change in the composition of ultra-thin Co(W) film, (3) Applicability to quantitative evaluation of barrier properties of oxygen or moisture barrier, (4) Applicability to trench structures.