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Growth Behavior and Diffusion Barrier Reliability of Manganese Oxide Formed by Chemical Vapor Deposition

著者	NGUYEN MAI PHUONG
号	56
学位授与機関	Tohoku University
学位授与番号	工博第4649号
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	ぬえん まい ふおん
氏　　　　　名	Nguyen Mai Phuong
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指　導　教　員	東北大学教授　小池　純一
論文審査委員	主査　東北大学教授　小池　純一　東北大学教授　田中　俊一郎 東北大学教授　一色　実

論文内容要旨

The feature size in advanced ultra-large scale integration circuits has been continuously scaled down to achieve high device performance. As the feature size is decreased, resistance-capacitance (RC) delay becomes a major limitation for device performance. To decrease the effective resistivity of interconnect lines, the thickness of the diffusion barrier layer should be reduced to a minimum possible value. According to the International Technology Roadmap for Semiconductor (ITRS), the anticipated barrier thicknesses are 2.4, 1.7 and 1.2 nm for the metal half pitches of 32, 22 and 16 nm, respectively, for intermediate-level interconnects in micro-processor units (MPU). The bilayer of Ta/TaN has been widely used as a diffusion barrier material for conventional Cu interconnects. However, the conventional barrier formation has begun to face technological limitations in the advanced technology node because the barrier layer thickness on the side wall of line trenches has become too thin to ensure the barrier property.

As a possible solution to this issue, Koike et al. have reported the self-formation of a Mn oxide diffusion barrier by sputter deposition of a Cu-Mn seed layer on tetraethylorthosilicate (TEOS)-SiO_2 substrates and subsequent annealing at 250 to 450 °C to create a reaction between Mn and SiO_2. This Mn oxide layer was formed during annealing by thermal reaction between Mn and SiO_2. The self-formed Mn oxide layer acted as an excellent barrier layer and its thickness could be controlled in the range of 2-8 nm. However, the sputtering method suffers from poor step coverage and will encounter difficulty as the technology node is advanced beyond 32 nm. In order to circumvent the step coverage problem, chemical vapor deposition (CVD) of Mn oxide can be utilized as an alternative technique.

The deposition of bis(ethylcyclopentadienyl)Mn, $(EtCp)_2Mn$, on SiO_2 formed a conformal layer of the Mn

oxide with a uniform thickness of 3 to 4 nm within a high aspect ratio contact hole. Neishi et al. used a precursor of $(EtCp)_2Mn$ and investigated the deposition behavior of Mn oxide with thermal CVD. They found that a thin amorphous Mn oxide layer was formed above 100 and below 400 °C, while metallic Mn islands were formed at 500 °C. Excellent barrier properties of the Mn oxide layer were reported after annealing at 400 °C for 100 h and after bias temperature annealing up to 3 MV/cm for 6 x 10^3 s at 277 °C. From these reports, CVD Mn oxide is thought to be a good candidate as a diffusion barrier layer for advanced interconnects.

Meanwhile, dielectric materials may contain moisture. The moisture type and amount depend on process conditions of the dielectric materials. When the SiO_2 substrates are subjected to annealing at elevated temperatures, the adsorbed water would be desorbed from the substrates. Due to the difference in the binding energies of each moisture type, the amount and type of residual moisture can vary. This allows us to investigate the moisture effects on the formation behavior of Mn oxide. Secondly, to decrease RC delay, low-k dielectrics has been used such as SiOC with k-value of about 2.8 or porous SiOC with k-value less than 2.2. In the device performance, the trend and via structures are formed by plasma etching. During process, SiOC will be damaged by plasma and surface of SiOC change from hydrophobic to hydrophilic. Therefore, the effect of plasma treatment and effect of moisture to Mn oxide formation are necessary to investigate. Thirdly, the formation location of Mn oxide layer is important information, whether on the top of dielectric layer or within the dielectric layer. If the barrier layer formed on the top of dielectric layer, the barrier layer has no influence on capacitance value, but the resistance value is influenced. On the other hand, if the barrier layer formed within the dielectric layer, the barrier layer has no influence on resistance value but capacitance value is influenced. Fourthly, the barrier property of Mn oxide is evaluated by thermal annealing. The $Cu/MnO_x/SiO_2/Si$ MOS structure is used to evaluate barrier property with different structures and thicknesses of MnO_x layer.

In this thesis work, substrates were TEOS-SiO_2, thermal-SiO_2, pristine SiOC, plasma treated SiOC and bare-Si. For the study of the moisture effect to the Mn oxide formation, some substrates were pre-annealed at various temperatures from room temperature to 500 °C in vacuum of 1.0 x 10^{-5} Pa for 30 min or 1 h using an infrared furnace. For the study of the plasma treatment effect to the Mn oxide formation, some pristine SiOC substrates were plasma treated at room temperature using different gases such as Ar, N_2 and O_2 for different times at a plasma power and frequency of 50 W and 13.56 MHz, respectively. Subsequently, on a substrate with or without pre-annealing or plasma treatment, a thin Mn oxide layer was deposited by CVD

at 200 or 300 °C for 30 min using H2 as a carrier gas and bisethylcyclopentadienyl manganese, $(EtCp)_2Mn$, as a precursor. In separate experiments, thermal desorption spectroscopy (TDS) was carried out to determine the type and quantity of moisture desorbed from the substrates during the annealing process at various temperatures. The adsorbed moisture in the substrates was measured by FTIR spectroscopy in the range of 400- 4000 cm^{-1}. The microstructure and thickness of the CVD-Mn oxide layer were investigated by transmission electron microscopy (TEM). X-ray photoelectron spectroscopy (XPS) measurement was also carried out using an angle-resolved mode at various detection angles from 28.4 to 81.2° with intervals of 3.75° to analyze the chemical bonding states of the CVD-Mn layer. The carbon contamination was analyzed by Raman spectroscopy and SIMS depth profile. The tape test was used to evaluate the adhesion strength between Cu and MnO_x layer according to the Japanese Industrial Standards K5600-5-6. For the diffusion barrier property, Metal-Oxide-Semiconductor (MOS) structure of $Cu/MnO_x/SiO_2/Si$ was used. Samples were annealed at 400 °C for various times from 10 to 600 min. The interdiffusion of Cu into the substrate was evaluated by using TEM, C-V, I-V and SIM depth profile technique.

At first, the study placed emphasis on the adsorbed moisture in a hydrophilic SiO_2 substrate and investigated the effects of the adsorbed moisture on the formation behavior, structure and composition of the CVD Mn oxide layer. The SiO_2 substrates were pre-annealed at 150 to 500 °C for 1 h to control the type and amount of the residual adsorbed moisture. A Mn oxide layer was subsequently deposited by thermal CVD of bis(ethylcyclopentadienyl)Mn at 200 °C for 30 min. The Mn oxide layer deposited on an as-received substrate was composed of the bilayer of crystalline MnO_x and amorphous $MnSi_xO_y$. The Mn oxide layer deposited on a pre-annealed substrate was composed of the single layer of amorphous $MnSi_xO_y$. The crystalline MnO_x layer was formed by the reaction of the Mn precursor with physisorbed moisture on the as-received SiO_2. The amorphous $MnSi_xO_y$ was due to the reaction with chemisorbed moisture on both the as-received and the pre-annealed SiO_2.These results indicate the importance of controlling the adsorbed moisture of the substrates in order to obtain a Mn oxide layer with desired structure and thickness as a diffusion barrier layer.

Next, the dependence of Mn oxide formation on plasma treated SiOC substrate was investigated. The CVD MnO_x layer can be formed on plasma treated SiOC substrate using different gases such as Ar, O_2 and N_2, but not on pristine SiOC substrate. The reason for the formation of MnO_x layer is the moisture adsorbed to the substrate after plasma treatment process. The structure and thickness of MnO_x were dependent on plasma treated gas and time. On the other hand, the Mn oxide formation was affect on the type and amount

of remained moisture in the plasma treated SiOC substrate. Below 180 °C of pre-annealed temperature, the MnO_x layer was composed of a bilayer of crystal on the top surface and amorphous on the bottom adjacent to the SiOC substrate. Above 180 °C of pre-annealed temperature, the MnO_x layer was composed of a single amorphous layer. The crystal and amorphous layer were formed by the reaction of the precursor and physisorbed or chemisorbed moisture, respectively.

The location of MnO_x formation is analyzed by the comparison the thickness of SiOC with and without MnO_x deposition. Two kinds of samples were prepared which are as-treated and pre-annealed samples at 300 °C for 30 min. In the both of samples, the thicknesses of SiOC without MnO_x layer were thicker than that with MnO_x layer which indicate the formation of CVD-MnO_x layer within the SiOC substrate. This result suggests that the barrier layer has no influence on the resistance of the metal lines, but influence on the capacitance of the dielectric layer.

The diffusion barrier property was investigated by thermal annealing test with various structures and thicknesses of MnO_x layer. The Cu/MnOx/SiO_2/Si/Al (MOS) structure samples were used and then samples were annealed at 400 oC for various times from 10 to 600 min in vacuum. The single amorphous of MnO_x with thickness of 1.2 nm showed a good diffusion barrier only for 10 min and failed for 60 min due to detecting Cu peak in the substrate region of EDS spectra. This MnO_x thickness is too thin to become a diffusion barrier layer. On the other hand, the a single amorphous with thickness of 2.0 nm or a bilayer of crystal and amorphous with thickness of 3.5 and 6.5 nm showed a excellent diffusion barrier up to 600 min due to no appearance of Cu peak in EDS spectra, no observation of flat band voltage shift and low leakage current maintenance in the annealed samples.

The calculation of the dielectric constant of dielectric layer including the barrier layer is performed. The dielectric constant of the dielectric layer including a single amorphous MnO_x is smaller than that of the dielectric layer without MnO_x layer. On the other hand, the dielectric constant of the dielectric layer including a bilayer of crystal and amorphous MnO_x is larger than that of the dielectric layer without MnO_x layer. The results indicated that the amorphous MnO_x barrier layer reduced the effective dielectric constant value or reduce RC delay. Therefore, the amorphous MnO_x layer is considered to be a good material for diffusion barrier layer.

According to these results, the manganese oxide layer formed by chemical vapor deposition is a good diffusion barrier material for Cu interconnects application.

論文審査結果の要旨

本研究は、先端半導体の多層配線構造の微細化を推進するにあたって技術的な重要課題となっている、拡散バリア層に関する研究である。現状の拡散バリア層はTa/TaNあるいはTi/TiNの二層構造を用いているが故に、Cu配線部分を占有するため配線の実効抵抗が増加し、配線遅延が悪化するという問題がある。膜厚を減少することが唯一の解決法であるが、拡散バリア性が犠牲になるため実現できていない。一方で、Cu-Mn合金を用いて加熱処理を行うことにより、Mnと絶縁層酸化物（SiO2）が反応してMnSiO3層が形成され、優れた拡散バリア性を示すことが報告されている。しかし、Cu-Mn合金はスパッタ法で成膜されるため段差被覆性が悪く、配線幅が狭い先端デバイスのプロセスには適していない。これに対して、本研究は段差被覆性に優れる化学気相成長（CVD）法を用いて$MnSiO_3$層を形成する方法を確立し、先端デバイスプロセスに適合する拡散バリア層の形成方法を提供することを目的とした。

CVD成膜に用いた有機金属前駆体は成膜温度における蒸気圧などを勘案して、bisethylcyclopetadienyl manganese, $(EtCp)_2Mn$を選択した。基板はSiO_2またはSiOCとした。成膜温度を変化して膜構造を調査した結果、500℃以上において金属Mn層が形成され、前駆体の熱分解温度が500℃近傍にあることが判明した。400℃以下においては酸化物層が形成され、その構造と組成は、基板に吸着する水分種と量に依存した。TDSによる分析の結果、受け入れままの基板には物理吸着水と化学吸着水が存在しており、150℃以上で前熱処理をすると化学吸着水のみが存在した。Mn前駆体は物理吸着水と反応して結晶性のMnOとなり、化学吸着水と反応して非晶質の$MnSiO_3$となった。基板の前熱処理の増加に伴って、化学吸着水の残留量が減少するため、非晶質$MnSiO_3$の膜厚も減少した。

種々の温度で成膜したMn酸化物層についてCuを上部電極としたMOS構造を作製し、高温長時間加熱ならびにBTSを行った後にC-V測定を行った結果、フラットバンド電圧に変化は見られず、Mn酸化物層が優れた拡散バリア性を有していることが明かになった。この結果はTEM-EDS, SIMSでも確認できた。また、断面TEM観察によって絶縁層基板と酸化物層の厚さ変化を測定した結果、酸化物層の成長に伴って絶縁層が薄くなっており、酸化物層が絶縁層内部に形成されたことを示した。従来のバリア層は絶縁層上に形成されCu配線の一部を占有したため、バリア層の電気抵抗を低減することが課題であったが、新しいバリア層は絶縁層の一部を占有することから、バリア層の比誘電率が重要な因子になることが明かになった。

さらに、バリア層とCu薄膜の密着強度を調査した。密着強度は配線構造の力学的信頼性だけでなく、エレクトロマイグレーションにも関連する重要な因子である。テープテストと四点曲げ試験の結果、400℃以上で成膜した酸化物は前駆体由来の炭素を多く含有しており、Cuが酸化物から容易に剥離した。一方で300℃以下で成膜した酸化物の炭素含有量は極端に少なく、良好な密着性を示した。400℃で多くの炭素を含有する原因を理解するために、第一原理法を用いて前駆体の各構成要素間の結合エネルギーを計算した。その結果、Mnの脱離エネルギーに比べてメチル基のそれは、やや小さく、Mnの脱離温度より少し低い温度においてメチル基が脱離しうることが明らかになった。このことから、400℃においては脱離したメチル基が酸化物膜に混入することが明かになった。

以上の結果は、今後のシリコン半導体の進展において非常に困難と思われていた拡散バリア層形成技術の課題に対して、明確な解を与えるものであり、学術的重要性はもちろんのこと、技術的にも多大な注目を集めている。

よって、本論文は博士(工学)の学位論文として合格と認める。