Materials Science in Semiconductor Processing xx (xxxx) xxxx–xxxx

Contents lists available at ScienceDirect

Materials Science in Semiconductor Processing

journal homepage: www.elsevier.com/locate/mssp

Effect of substrate type and temperature on the growth of thin Ru films by metal organic chemical vapor deposition

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ARTICLE INFO

Keywords:
Ruthenium
Thin films
MOCVD
(2,4-Dimethylpentadienyl)
(ethylcyclopentadienyl)ruthenium

ABSTRACT

Ru thin films were deposited by pulsed metal organic chemical vapor deposition at 210 °C and 300 °C on SiO_2 (native oxide)/(001)Si, HfSiON/SiON/(001)Si, and HfO_2/SiON/(001)Si substrates from (2,4-dimethylpentadienyl)(ethylcyclopentadienyl)ruthenium [Ru(DMPD)(EtCp)]–O_2. The effects of substrate and deposition temperature on the deposition of Ru thin films were investigated. The incubation time, the period in which film deposition was hardly observed at the early deposition stage, strongly depended on the substrate and the deposition temperature. In addition, incubation time and the deposition rate after the incubation time were almost independent of the Ru precursor concentration at 300 °C, suggesting that the deposition rate is limited by the surface reaction. Atomic force microscopy observations revealed that the average surface roughness, *Ra*, of the films deposited at 300 °C was lower than those deposited at 210 °C for all substrates. It was also clear that the *Ra* increased significantly with increasing incubation time. In addition, the film deposited at 300 °C showed lower resistivity than that deposited at 210 °C. These results clearly show that the Ru films deposited at 300 °C on SiO_2 (native oxide)/(001)Si, HfSiON/SiON/(001)Si, and HfO_2/SiON/(001)Si substrates show shorter incubation times with smoother surface and lower resistivity than those at 210 °C.

1. Introduction

Ruthenium (Ru), in the form of thin films, has been widely investigated as an electrode metal for dynamic random access memories [1], as a gate metal in metal-oxide-semiconductor field-effect transistors [2], and the seed layer material for copper interconnects, due to its low resistivity, relatively high work function, and low diffusivity with various materials.

Thin film deposition of Ru by metal organic chemical vapor deposition (MOCVD) and atomic layer deposition have been widely investigated [3–25] due to their ability to deposit thin films with good conformability at relatively low temperatures. Our groups reported the effect of the incubation time, the time period in which the film deposition was hardly observed at the early deposition stage, for Ru film deposition at 210 °C on various kinds of substrates by pulsed MOCVD from (2,4-dimethylpentadienyl)(ethylcyclopentadienyl)ruthenium [Ru(DMPD)(EtCp)]–O_2 and bis(2,4-dimethylpentadienyl)ruthenium [Ru(DMPD)$_2$]-O_2 [3]. Results obtained indicate that a shorter incubation time results in smoother and thinner continuous films. However, details of the film characteristics deposited at different temperatures were not investigated.

In this study, Ru(DMPD)(EtCp) was selected as the Ru source to deposit Ru films by pulsed MOCVD to further investigate the effects of substrate and the deposition temperature on the deposition behavior of Ru films.

2. Experimental procedure

2.1. Film deposition

Metallic ruthenium films were deposited by pulsed MOCVD at 210 °C and 300 °C at low pressure (130 Pa) from Ru(DMPD)(EtCp)-O_2. Ru(DMPD)(EtCp) (Tosoh Corporation) was used as the Ru precursor, while oxygen gas was used as the oxygen source. Deposition temperatures of 210 and 300 °C were selected; these two temperatures were respectively located at the lower- and higher-temperature regions in the relationship between the logarithm of the deposition rate after incubation and the inverse of the temperature (Fig. 5 of reference [3]).

Ru thin films were deposited as per the following procedure. The substrates were placed on the heater stage in the reaction chamber, and this stage was heated to the desired temperature (210 °C or 300 °C).

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http://dx.doi.org/10.1016/j.mssp.2016.11.032
Received 12 July 2016; Received in revised form 14 November 2016; Accepted 17 November 2016
Available online xxxx
1369-8001/

During this heating step, oxygen and nitrogen gases were continuously introduced into the chamber without Ru precursor flow. The total pressure was kept at 130 Pa, and the partial pressure of oxygen gas was 1.3 Pa. Heating was performed at the rate of 10 °C/min until the desired temperature was achieved. After the stage temperature reached the set temperature, the temperature was stabilized for 10 min. The deposition started with the introduction of the Ru precursor and oxygen gas into the chamber. The pulsed Ru precursor injection cycle lasted a total of 15 s and consisted of two steps: Ru precursor injection into the chamber for 10 s and Ru precursor exhaust (without introducing into the chamber) for 5 s. This injection cycle was repeated until completion of the deposition. The Ru precursor was vaporized by bubbling with nitrogen gas at a flow rate of 0.056 or 0.126 cm^3/min. During the deposition, the total pressure and oxygen gas pressure were kept constant at the same level as before film deposition. When the deposition was finished, the introduction of the Ru precursor into the reactor was stopped, the atmosphere of the chamber was maintained steady, and the stage was cooled down to room temperature at 10 °C/min.

It must be noted that the deposition time in this study is defined as the time from the starting point to the end point of the Ru supply (including the time when the Ru source was pulsed off). Therefore, the actual Ru source supply time is only two-thirds of the total deposition time. The dependences of the deposition amount on the Ru supply time and the interval time are under investigation; the discussion of the present study uses the total deposition time.

Three substrates with amorphous top layer having various Hf/Si ratios were used for Ru thin film deposition: SiO_2 (native oxide)/(001)Si, HfSiON/SiON/(001)Si, and HfO_2/SiON/(001)Si. In this study, these substrates are abbreviated as SiO_2, HfSiON, and HfO_2, respectively. HfO_2- and SiO_2-top (001)Si were selected as substrates to demonstrate Ru-electrode film deposition as a gate metal in metal-oxide-semiconductor field-effect transistors. On the other hand, HfSiON substrate was also used to investigate the effect of substrates that have different Hf/Si ratios on the deposition characteristics and Ru thin film properties. The experimental substrate size was 10 mm×10 mm, and the average surface roughness (*Ra*) of the three kinds of substrates measured by atomic force microscopy (AFM) was 0.39 nm, 0.24 nm, and 0.12 nm for the SiO_2, HfSiON, and HfO_2 substrates, respectively.

2.2. Film characterization

The amount deposited was estimated by X-ray fluorescence (XRF). The amounts of Ru atoms in the deposited Ru films were calculated from the X-ray intensities of elemental Ru, against the response calibrated using standard samples. It was already ascertained by XRD measurements that all deposited films were metallic ruthenium, as only the diffraction peaks of metallic ruthenium were detected. In the case of the continuous film, the physical thickness was ascertained to be equal to 130 nm measured by surface profile measurement when the deposition amount was 10×10^{-7} mol/cm^2. The *Ra* was obtained from a 5 μm ×5 μm square area observation using AFM to evaluate film flatness. The error bar on *Ra* that corresponds to the standard deviation was estimated to be less than 10%.

A standard direct-current four-probe method was used for the measurement of apparent resistivity at room temperature. The apparent resistivity was calculated from the measured resistance and the film thickness (estimated by the deposition amount of the Ru film, assuming that the film density was equal to that of bulk ruthenium and the film surface was completely flat). It must be mentioned that the standard deviation of the apparent resistivity in Fig. 6 was within 5%.

3. Results and discussion

Fig. 1(a)–(c) show the dependence of deposition amount on deposition time for the Ru films deposited at 210 and 300 °C on the various substrates with the Ru precursor flow rate at 0.056 cm^3/min.

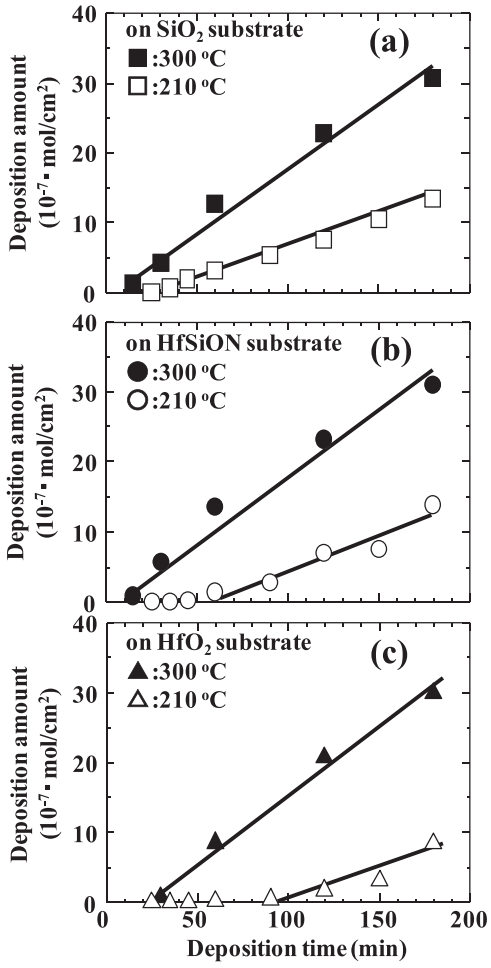

Fig. 1. Dependence of deposition amount for Ru films on deposition time at 210 °C (open symbols) and 300 °C (closed symbols), respectively on (a) SiO_2 (native oxide)/(001)Si [SiO_2], (b) HfSiON/SiON/(001)Si [HfSiON], and (c) HfO_2/SiON/(001)Si [HfO_2] at a Ru precursor flow rate of 0.056 cm^3/min.

As shown in Fig. 1, there is an incubation time (the period in which film deposition is hardly observed) at the early deposition stage. After the incubation time, amount deposited increased almost linearly with deposition time for all cases. A strong dependence of the incubation time on the deposition temperature and the substrate was observed.

The incubation time estimated from Fig. 1(a)–(c) is summarized in Fig. 2(a). The incubation time of the films deposited at 300 °C was shorter than that deposited at 210 °C for all substrates. Moreover, incubation time became longer in the case of the substrates with larger surface Hf/Si ratio at both deposition temperatures. These results show that the incubation time strongly depended on the deposition temperature and the Hf/Si ratio of the substrate surface. Fig. 2(b) shows the deposition rate after incubation for the same Ru films as in Fig. 2(a). It is clear that the deposition rate for the films deposited at 300 °C was significantly higher than those deposited at 210 °C. However, the deposition rate was almost independent of the substrate at both deposition temperatures. This strong dependence of the deposition rate after the incubation time on the deposition temperature implies that the deposition rate is limited mainly by the surface reaction step instead of the diffusion step of the reaction species on the reaction surface.

To investigate the rate limiting step in detail, the deposition amount as a function of deposition time was measured at the source gas supply rates of 0.056 cm^3/min and 0.126 cm^3/min for films deposited at