Extended Abstracts of the 2002 International Conference on Solid State Devices and Materials, Nagoya, 2002, pp. 172-173

B-3-3

Improvement of electrical properties for high-κ dielectrics grown by MOCVD via cyclic remote plasma oxidation

Sadayoshi Horii[1], Masayuki Asai[1], Hironobu Miya[1]
Kazuhiko Yamamoto[2], and, Masaaki Niwa[2]

[1] Semiconductor Equipment System Laboratory, Hitachi Kokusai Electric Inc.
2-1 Yasuuchi, Yatsuo-Machi, Nei-gun, Toyama, 939-2393, Japan
Phone:+81-76-455-9132, Fax:+81-76-455-9147, E-mail: horii.sadayoshi@h-kokusai.com
[2] ULSI Process Technology Development Center, Matsushita Electric Industrial Co., Ltd.
19, Nishikujo-Kasugacho, Minami-ku, Kyoto, 601-8413, Japan

1. Introduction

The metal organic chemical vapor deposition (MOCVD) technique for high-κ gate dielectrics has been widely studied with much attention focused on HfO_2 and ZrO_2 [1,2]. However, there have been some difficulties, such as carbon contamination and rough surface due to incubation time, on these thin films prepared by MOCVD. On the other hand, atomic layer deposition (ALD) also has been extensively studied due to the promise of the control of thickness, uniformity, quality and material properties [3]. However, the films prepared by ALD at lower temperature also have problems of Cl and H contaminations [3,4]. In this paper, we discuss the chemical reaction of MOCVD deposition based on the experiment, and the advantage of remote plasma oxidation (RPO) for improving the film quality, and propose a new CVD method, which reduces the incorporation of impurity and improves the electrical property.

2. Experimental procedure

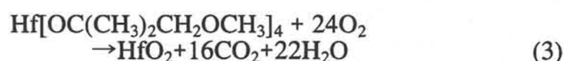
The HfO_2 film was deposited in a reactor with ports for vaporized metal organic (MO) precursor and remote oxygen plasma. The MO precursor used in this experiment is $Hf\text{-}(MMP)_4$ ($Hf[OC(CH_3)_2CH_2OCH_3]_4$). The MOS capacitor structure for measuring the C-V and the I-V characteristic is prepared as follows. The Si surface was treated by NH_3 at 600°C for 30 sec, prior to the HfO_2 deposition. Some samples were treated by RPO after the HfO_2 deposition. The TiN layer was deposited by CVD on the HfO_2 films after the post deposition anneal at 650°C for 15 min in N_2, and was defined by photolithography and etching to form the MOS electrode. The capacitance equivalent thickness (CET) of the HfO_2 films was obtained from the capacitance value at Vg = -3 V. The I-V characteristic was measured at 100°C. The electrode areas for the C-V and the I-V measurements are 10000μm^2 and 1000μm^2, respectively.

3. Results and Discussion

Figure 1 shows the substrate temperature dependence of deposition rates by MOCVD with and without oxygen addition. It is found that the deposition rate of HfO_2 with O_2 is larger than that without O_2, and the activation energy of the deposition with O_2 is smaller than that without O_2. This means that the mechanism of the deposition with O_2 is different from that without O_2. It is speculated that the molecular reactions of the MOCVD deposition without O_2 are thermal reaction that is shown by eq. (1) and (2). On the other hand, the reaction with O_2 is an oxidation reaction shown by eq. (3). In these reactions, eq. (1), (2) and (3) are endoergic reaction, and the endoergic energy in eq. (1) is larger than that in eq. (3). From these facts, it is supposed that the activation energy of the deposition with O_2 is smaller than that without O_2. Also, as shown in eq. (3), it is found that much of CO_2 and H_2O are generated from the reaction with O_2 during the deposition, and it seems possible that these subsidiary products may be incorporated in the HfO_2 film. However, from the reaction without O_2, number of the generated molecular counts of alcohol and H_2O are less than the case with O_2 during deposition. From this, deposition without O_2 is expected to less incorporate the impurity than the case with O_2.

$$Hf[OC(CH_3)_2CH_2OCH_3]_4 \rightarrow Hf(OH)_4 + 4C(CH_3)_2CH_2OCH_2 \qquad (1)$$

$$Hf(OH)_4 \rightarrow HfO_2 + 2H_2O \qquad (2)$$



$$Hf[OC(CH_3)_2CH_2OCH_3]_4 + 24O_2 \rightarrow HfO_2 + 16CO_2 + 22H_2O \qquad (3)$$

Figure 2.(a), (b), and (c) show the thermal desorption spectroscopy (TDS) of the 30 nm-HfO_2 film deposited on the Si substrate without O_2, with O_2, and the RPO-treated 30 nm-HfO_2 film after the deposited without O_2, respectively. From figs. 2 (a) and (b), it is found that the HfO_2 film deposited without O_2 includes larger amount of H_2 than that with O_2. It is supposed that the hydrogen comes from $-OH$ which does not fully react into HfO_2 in eq. (2). It is also found that the HfO_2 film deposited with O_2 includes larger amount of H_2O and CO than that without O_2. This result is agreeable with the reaction as shown in eq. (1) and (3), and shows that the deposition condition without O_2 are effective in reducing the contamination of CO and H_2O. In order to reduce the contamination by H and H_2O, the HfO_2 film (fig. 2(c)) was exposed to the remote O_2 plasma. From figs. 2 (a) and (c), it is found that the amount of H_2 and H_2O in the HfO_2 film are reduced by RPO. From these results, although it is found that 30 nm-HfO_2 is too thick to completely remove H_2O and H_2, the RPO-treatment is effective to reduce the H and H_2O contaminants.

Figure 3 shows the O_2 flow rate dependence of CET and break down voltage of the 5 nm-HfO_2 film deposited without RPO treatment. From this figure, because it is found that the CET does not change but the breakdown voltage on I-V measurement decreases with increasing O_2 flow rate, the contaminant such as C or H_2O is considered to influence the leakage current.

Figure 4 shows the RPO time dependence of CET and leakage current density of 5 nm-HfO_2 films. From this figure, it is found that the CET does not change but the leakage current decreases with increasing the RPO time. This indicates that the RPO treatment dose not increase the thickness of the interface layer between the HfO_2 film and the Si substrate, but improves the film quality. From these discussions, it becomes apparent that HfO_2 deposition without O_2 is effective to suppress the C and H_2O

contamination, and the RPO treatment is effective to remove the hydrogen from the HfO_2 film without increasing the interface layer thickness, so that we propose the MOCVD of HfO_2 via cyclic RPO treatment. The detail of the method is as follows: 1) MO precursor is introduced with vaporizing for a few or some atomic layers deposition. In this phase, if the substrate temperature is higher than that for the material decomposition, the reaction in eq. (1) will occur. 2) Remote oxygen plasma is irradiated on the deposited layers. We speculate the remote oxygen plasma may assist the reaction in eq. (2), and removes the contaminant from the films as observed in fig. 2(c). 3) These process are repeated until the film thickness reaches to the desired value. Here, the substrate temperature should be higher than the decomposable temperature (~ 270°C) of the precursor, unless the contaminant such as H and CO will increase. At the lower temperatures the MO precursor will still remain without decomposing and the reaction in eq. (3) will occur.

Figure 5 shows the substrate temperature dependence of a deposition rate by the cyclic method. Although, at the substrate temperature of 300°C, the deposition rate per cycle is 0.06 nm that is similar to ALD [3], and the deposition rate per cycle increases 0.9 nm at 425°C. Because the activation energy of this method is different from conventional MOCVD method in fig. 1, the chemical reaction of the deposition by the cyclic method seems to be different from that for conventional MOCVD.

Figure 6 shows the relationship between CET and leakage current density of the HfO_2 capacitor deposited by MOCVD and the cyclic method at substrate temperature of 425°C. Prior to the HfO_2 film deposition, the interface layer of 0.8 nm was formed by NH_3 annealing. The physical thickness of the HfO_2 films is 2.3, 3.1, 3.8, and 4.6 nm, respectively. From fig. 6, it is also found that the leakage current density of the HfO_2 film by the cyclic method is 1/100 of the film by the conventional MOCVD. From these results, it is clarified that the film quality is improved by the cyclic RPO treatments.

4. Conclusions

We demonstrated the difference of the chemical reaction of MOCVD deposition with and without O_2, and the advantage of RPO for improving the film quality. Also, we proposed new cyclic CVD method that repeats MO precursor introduction and RPO. Furthermore, we show that the cyclic method is effective to lower the leakage current and thinner CET. Further improvements for the CVD-HfO_2 gate dielectrics can be realized by means of this method.

References

[1] E. P. Gusev et.al., IEDM Tech. Dig. p.451, 2001.
[2] Y. Kim et.al., IEDM Tech. Dig. p. 455, 2001.
[3] O. Sneh et.al., Thin Solid Films **402** (2002) 248.
[4] S. J. Yun et.al., J. Korean Phys. Soc. **33** (1998) S170.

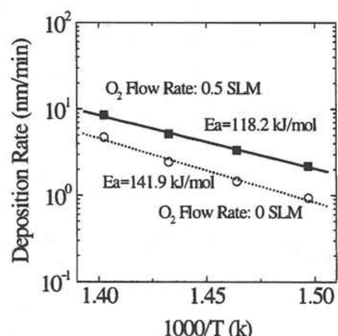


Fig. 1 The substrate temperature dependence of a deposition rate by MOCVD with oxygen addition and without oxygen addition.

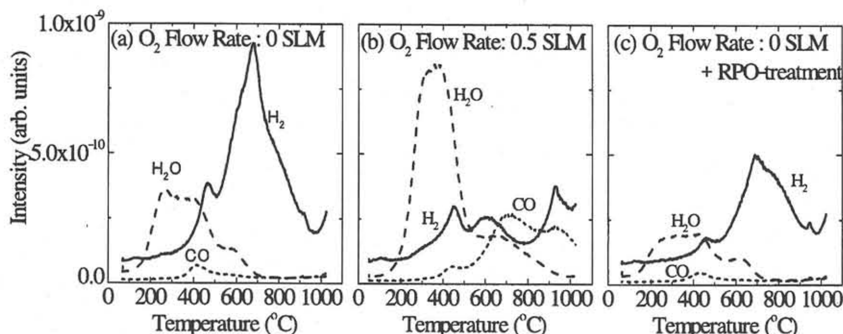


Fig. 2 The thermal desorption spectroscopy (TDS) of the 30 nm-HfO_2 film deposited on the Si substrate (a) without O_2, (b) with O_2, and (c) the RPO-treated 30 nm-HfO_2 film deposited without O_2.

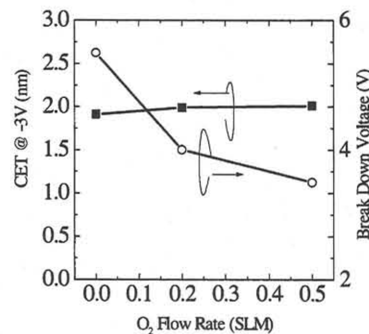


Fig. 3 O_2 flow rate dependence of CET and break down voltage of the 5 nm-HfO_2 film deposited by MOCVD.

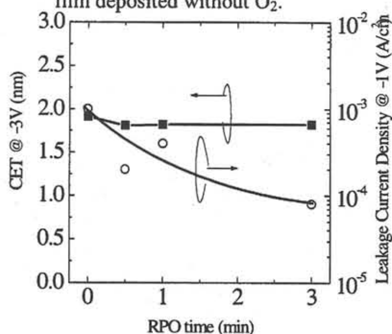


Fig. 4 The RPO time dependence of the CET and leakage current density of 5 nm-HfO_2 deposited by MOCVD.

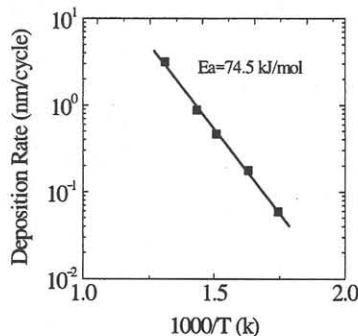


Fig. 5 The substrate temperature dependence of a deposition rate by the cyclic method.

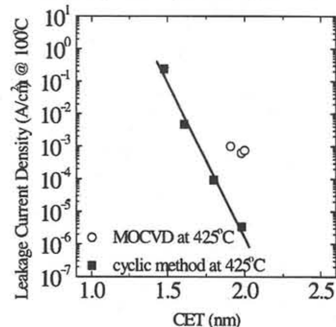


Fig.6 The relationship between CET and leakage current density at −1V. The IV characteristic was measured at 100°C.