論文題目　Synthesis and characterization of HfN-based metal gate electrodes by MOCVD for the application of advanced High-κ MOS stacks

（MOCVD 法を用いた High-κ MOS スタック用 HfN 系金属電極の合成と評価）

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本文）：

1. Introduction

With the aggressive dimension shrinkage of complementary metal oxide semiconductor (CMOS) transistor device, the gate stack related material integration becomes the most critical issues. Especially, for the sub-0.1 μm CMOS technology, high-κ dielectric and gate metal electrode are currently under consideration as potential replacements for SiO_2 and polysilicon as the gate dielectric and gate electrode materials to resolving the problems associated with CMOS stack such as the tunneling leakage current, boron penetration and the depletion in the polysilicon electrode. Metal gates offer a possible solution to the boron diffusion, polysilicon gate depletion, sheet resistance constrains and even the required thermal budget for a dopant activation anneal in the polysilicon electrode.

In this work, we have mainly focused our attention on the study about the gate metal electrode, especially on the synthesis and characterization of Hf-based nitride films by MOCVD technique for meeting the requirements both for alternative gate material and for CVD fabrication technique. Regarding hafnium nitride (HfN), it is one of the most promising candidates to replace the conventional polysilicon electrode because of its superior properties such as low bulk resistivity of 33 μΩ-cm, appropriate mid-gap work function and expected high thermal stability (melting point: 3330 ^{o}C). In addition, the CMOS device integration might also be simplified when HfN gate electrodes are used, because by changing the oxidizing agent to a nitriding agent, HfN/HfO_2/Si MOS gate stack can be integrated in the same chamber by using CVD/atomic layer deposition (ALD) with the same precursor.

2. Main subject

2.1 Fabrication of HfN_x films with low levels of C and O impurities but high resistance by using TDEAHf precursor and NH_3 gas

In this section, sample synthesis was carried out by metal organic chemical vapor deposition (MOCVD) method. It was found that HfN_x films with low levels of carbon (<0.1 at.%) and oxygen (~2 at.%) impurities were fabricated by MOCVD technique using $Hf[N(C_2H_5)_2]$ (TDEAHf) precursor and NH_3 reducing gas. And high-κ Hf silicate phase was confirmed to form at the interface of HfN_x and SiO_2 underneath during HfN_x deposition, and the growth of Hf silicate phase seems to be independent of the growth temperature and the length of growth time, but greatly depend on the precursor partial pressure. This result suggests the potential possibility to control the gate interfacial region if HfN gate can be practised in MOS integration. On the other hand, regarding the electrical property of the HfN_x films, it shows strong dependence on the film composition. Despite the low levels of impurities, the as-deposited films behave high-resistivity characteristic (the order of 10^9 μΩ-cm) due to the excessive N content (N/Hf: 1.39), which resulted in the formation of insulating N-rich nitride, e.g., Hf_3N_4; furthermore after *ex-situ* Ar^+ bombarding, the resistivity was decreased greatly by more than 5 orders of magnitude, due to the N depletion originating from the selective etching of N, which induced a thin $HfN_{<1}$ surface conductive layer (~1 nm) This phenomenon is regardless of the various experimental conditions.

Summarizing the above results, both the NH_3 reductant and *ex-situ* Ar^+ ions bombarding play a decisive role in synthesizing metal hafnium nitrides using CVD technique. Thus considering the strong reducing characteristic of NH_3 and the promising ability of Ar^+ ions bombarding in controlling N content, we propose that plasma-assisted MOCVD or ALD approaches by employing NH_3 reductant could be capable of synthesizing hafnium nitrides ($HfN_{\leq 1}$) with both low impurities and low resistivity.

2.2 Fabrication of conductive HfCN films by NH_3-free growth using TDEAHf precursor

According to the descriptions above, N content is a decisive factor to the electrical resistance property of Hf nitride films. The key point to synthesize conductive Hf nitrides is to control the atomic ratio of N to Hf to be less or close to one, i.e., $HfN_{\leq 1}$. However, although a conductive surface layer could be induced by Ar^+ ions bombarding to the films formed with NH_3 gas, it is only localized on the top surface, which thereby limits its further application as a metal gate electrode in MOS stacks. Therefore, alternative experimental approaches to decrease the resistivity of the as-deposited films need to be explored. In this section, we described a NH_3-free growth for conductive Hf-based nitride, i.e., hafnium carbonitride (HfCN).

Metallic Hf-based nitride films were synthesized by MOCVD using NH_3-free growth, i.e., without NH_3 addition during film growth. Due to the incorporation of a large amount of C, especially the formation of HfC_x phase, the form of the films formed by NH_3-free growth was written into HfCN. The composition and electrical properties of the HfCN films showed strong dependence on growth temperature. At low temperatures, e.g, 300 ^oC, the films contain large number of O, and the resistivity was very high, larger than the order of 10^6 μΩ-cm; while with the increasing temperature, both the O content and resistivity of the films decreased significantly, especially above 600 ^oC, where metallic HfCN film was formed and the resistivity decreased to be about 10^4 μΩ-cm due to the formation of metallic HfN_x and HfC_x phases.

In this section, in order to further decrease the resistivity of the as-deposited HfCN films, experiments employing pulse injection of NH_3 was also examined considering the strong reduction characteristic of NH_3. As a result, even trace of NH_3 addition degraded the electrical resistivity of the HfCN films, suggesting its incapability in improving the electrical characteristic of the HfCN films formed by MOCVD.

2.3 Electrical property evaluation of HfCN metal electrode gated MOS stacks

The electrical and thermal stability characteristics of the HfCN films formed by NH_3-free growth were evaluated as metal gate electrode. The capacitance-voltage (C-V) measurements were carried out to perform electrical property evaluation using a C meter (Hewlett Packard) at 1MHz. As a result, 4.54 eV and 4.45 eV of midgap effective work function were extracted for the $HfCN/SiO_2/Si$ and $HfCN/HfO_2/SiO_2/Si$ MOS capacitors. For the $HfCN/SiO_2/Si$ structure, after RTA annealing in N_2 ambient, the *EOT* values show negligible change; while the flat band voltage shifted gradually with the RTA temperature. The Φ_{HfCN} was calculated to be about 4.78 eV and 5.08 eV after 800 ^oC and 900 ^oC RTA process, respectively. This might be attributed to the variations in structure and chemical composition, and even the possible atoms diffusion at the interfacial region.

2.4 Dielectric evolution characteristics of HfCN metal electrode gated MOS stacks

In this section, dielectric evolution characteristic of HfCN metal electrode gated MOS stacks was discussed, and efforts were attempted to evaluate the feasibility of *in-situ* integrating Hf-based metal/Hf-based high-k dielectric/Si MOS stack on SiO_2 by one step HfCN deposition. It was found that after HfCN deposition, *EOTs* become smaller than the initial *EOTs* of various dielectrics. For the case of $HfCN/SiO_2/Si$ stacks, the reduction in *EOTs* was attributed to the increase in average effective dielectric constant, due to atoms interdiffusion, e.g, N, Hf or O atoms, which may promote the formation of high-κ dielectric phases; while for the case of $HfCN/HfO_2/SiO_2/Si$ stacks, the reduction in *EOTs*, which is much smaller than that in $HfCN/SiO_2/Si$ stacks, was attributed to the formation of thin interlayer owning much high dielectric constant, possibly due to the N diffusion from precursor or formed HfCN phase into the oxide underneath. On the other hand, regarding the evaluation of *in-situ* high-κ integration by one step deposition mentioned above, the leakage current in $HfCN/SiO_2/Si$ stacks with reduced *EOTs* shows similar level to that in doped-polysilicon/SiO_2 stacks, indicating further study such as on synthesis approach or on precursor is necessary to realize this idea.

3 Conclusions

In summary, the synthesis and characterization of HfN-based metal electrodes by MOCVD for the advanced MOS devices were systematically investigated for the first time. Pure HfN_x films with low levels of carbon (<0.1 at.%) and oxygen (~2 at.%) impurities were prepared by MOCVD using TDEAHf precursor and NH_3 gas. Because of the high-content N in the films (atomic ratio of N to Hf: ~1.39), however, the as-deposited HfN_x films show high resistivity (about the order of 10^9 μΩ-cm), due to the possible formation of insulating Hf_3N_4 phase. By employing *ex-situ* Ar^+ ions bombarding, the resistivity of the high-resistance films was decreased at least 5 orders of magnitude because of the formation of thin surface conductive layer (atomic ratio of N to Hf: <1) due to the N depletion during Ar^+ ions bombarding. On the other hand, by employing NH_3-free growth, conductive HfCN films were directly produced. The composition and electrical properties of the HfCN films, however, strongly depend on the growth temperature, especially above 600 ^oC, the resistivity of films was decreased to the level of 10^4 μΩ-cm. The electrical and dielectric evolution characteristics of the HfCN films were evaluated. As a result, 4.54 eV and 4.45 eV of midgap effective work function were extracted for the cases of $HfCN/SiO_2/Si$ and $HfCN/HfO_2/SiO_2/Si$ MOS stacks; regarding the dielectric evolution, the large reduction in EOT for the case of $HfCN/SiO_2/Si$ stacks was attributed to the improved effective dielectric constant due to possible atomic interdiffusion, e.g., N, Hf or O. This result is expected to be contributing to *in-situ* integrating Hf-based metal electrode/Hf-based high-κ dielectric/Si MOS stacks by one step deposition on SiO_2 dielectric through further exploration.