Carbon-Free Tantalum-Nitride Film from Ammonia and Extremely Diluted Pentakis-dimethylamino-Tantalum; Effect of Silicon Incorporation to nMIS-FET Metal-Gate

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1. Introduction

Tantalum-nitride (TaN) is a promising material as a metal gate-electrode of future MIS-FET because of its chemical stability, diffusion barrier property and robustness against high temperature Si-LSI process (950-1050°C). The effective workfunction of TaN is corresponding to the mid gap of Si (~4.6eV). As a result, TaSiN_x compounds are usually used to n-MOS-FET applications as a conduction-band-edge workfunction metal because the Si incorporation lowers the film workfunction [1]. On the other hand, electron mobility degradation is a typical problem of metal-gate transistors. We found that the incorporation of Si into TaN also improves electron mobility in a Hf-based high-k (high dielectric constant gate-dielectrics) metal-gate transistor. In this paper, the mechanism of mobility improvement during Si incorporation is discussed comparing the results with TiN or TiSiN_x gate devices.

It is known that the chemical vapor deposition (CVD) of TaN is difficult because of the lack of appropriate CVD precursors. Most of source-materials such as halides show very low vapor-pressure and halogen incorporation problem. Typical high vapor-pressure metal-organic (MO) precursors give rise to severe carbon incorporation during CVD. We have established an MOCVD technology for carbon-free TaN and TaSiN_x films using with NH_3. Pentakis-Di-Methyl-Amino-Tantalum (PDMAT; Ta[N(CH_3)_2]_5) and SiH_4. This technology does not require any plasma activation. Deposition chemistry is also described concerning with vapor-phase reaction of these materials.

2. Experiments

CVD TaN was thermally deposited from NH_3 and PDMAT at the temperature ranging from 350°C to 500°C. PDMAT is solid low vapor-pressure material (Fig. 1). A special precursor bottle designed for solid material was used for stable source delivery and the partial pressure of PDMAT requiring five time fold substitution with the vapor-phase reaction between NH_3 and extremely diluted PDMAT could thus be negligible. We can conclude that the vapor-phase reaction between NH_3 and extremely diluted PDMAT can provide carbon-free TaN film.

As shown in Fig. 3, the film composition can be changed with wide range by the alternating deposition of TaN and Si. Effective workfunction estimated from CV characteristics (Fig. 4) decrease with the increase of Si composition in the films. The electron mobility of high-k/metal-gate transistors was improved with the increase of Si incorporation, as shown in Fig. 5. We found the similar phenomena with TiN or TiSiN_x gate transistor, as seen in Figs. 6 and 7. It is noticeable that the recovery of mobility accompanied with workfunction decreasing, with different gate-material or different gate-process transistor.

With Hf-based high-k transistor, Fermi-level-pinning is the biggest problem, especially when high temperature process is employed. The pinning position is thought to be at ~4.3eV and it is believed that the pinning is caused by some charge transfer between gate-metal and gate-dielectrics accompanied by some elemental transfer (e.g. O) during high temperature process [4]. Such charge transfer might degrade the channel mobility of high-k/metal-gate transistor. When the original workfunction of gate material is closed to be 4.3eV, any charge transfer would not be possible. We consider that Si incorporation into gate-metal might suppress the portion of charge transfer related to the Fermi-level-pinning at high temperature, as shown in Fig. 8. The model suggests that the best workfunction is ~4.3eV for n-MIS gate material.

3. Results and Discussion

In Fig. 2, the growth temperature dependences of Carbon and hydrogen residence in CVD-TaN, measuring by SIMS, were shown. Both the C and the H residence was extremely low (~0.5%) and those were decreased with the decreasing of the growth temperature. It was also confirmed that any thermal decomposition of PDMAT, without NH_3 film (C: ~30%). The results suggest the deposition of a carbon-free TaN film does not require thermal assistance, with all organic ligands of PDMAT being eliminated by NH_3 with high efficiency. Conventional reaction model of PDMAT and NH_3 involves a subsequent substitution reaction, with the elimination of five-ligands from PDMAT requiring five time fold substitution with NH_3. This does not realistically explain our results. We suppose, however, that the NH_3 can decompose PDMAT and create carbon-free Ta-fragment with one reaction. It must be also emphasized that the partial pressure of PDMAT was 10^-5 Torr under our deposition condition and the vapor phase reaction between PDMAT and its fragment could thus be negligible. We can conclude that the vapor phase reaction between NH_3 and extremely diluted PDMAT can provide carbon-free TaN film.

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4. Conclusion
A carbon-free MOCVD TaN film was prepared by the vapor phase reaction between NH3 and extremely diluted PDMAT. Si incorporation into the film provided good effective workfunction as n-MIS gate material. The Si incorporation also improved the channel mobility of Hf-based high-k MIS-FETs. It was noted that the mobility degradation in the high-k/metal-gate transistor could be related to the Fermi-level-pinning of Hf-based high-k dielectrics which modify the effective workfunction of gate-metal.

References