Work Function Engineering of Molybdenum Gate Electrodes by Nitrogen Implantation

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The continued scaling of complementary metal oxide semiconductor (CMOS) devices into the sub-70 nm regime will require a fundamental change in transistor gate stack materials. Refractory metals and their metallic derivatives are among the few materials other than poly-silicon suitable for use as metal oxide semiconductor field effect transistor gate electrodes. In this paper we report the dependence of the Mo gate work function on nitrogen implant dose and energy. By implanting nitrogen into Mo/SiO2/Si stacks, the interfacial Mo work function can be controllably lowered from an initial (unimplanted) value of ~5 eV. The ability to engineer the Mo gate work function over the range of the Si energy bandgap makes it an attractive candidate for future bulk-Si and ultrathin body silicon-on-insulator-CMOS gate electrodes.

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Results

Effective gate work functions were extracted using values of the flatband voltage (VFB) for capacitors with varying oxide thickness. This technique allows the metal-semiconductor work function difference (ΦM/SiO2) to be calculated free of the effects of oxide charge. Metal work function values (ΦM) obtained by this technique should be considered to be fair approximations after accounting for uncertainties in the determination of VFB and the contributions of interface trap states. The results of the above analysis are summarized in Fig. 1 which shows the effect of the nitrogen implantation on the C-V characteristics. It is clear that implantation induces a negative shift in the flatband voltage. Figure 2 indicates the variation of the measured Mo interfacial work function with implant dose and energy. It can be seen that a higher implant dose in general leads to a lower work function. This dose dependence is enhanced at higher implant energies. Annealing at 700°C leads to a significant lowering of the work function. Subsequent annealing at 900°C increased the work function, and further annealing at a lower temperature (400°C) was seen to have a negligible effect on the work function values. The low work function states obtained thus appear to be metastable ones. Figure 3 shows the results of secondary-ion mass spectroscopy (SIMS) analysis which indicate the variation of the nitrogen content in the Mo film with annealing. While the as-


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implanted profile shows no distinct features, a significant pileup of nitrogen is observed at the Mo/SiO\textsubscript{2} interface after annealing at 700°C. This segregation effect is even more prominent after annealing at 900°C. Figure 4 shows the results of X-ray diffraction (XRD) analysis performed on the Mo/SiO\textsubscript{2}/Si stack after implantation. The broad diffraction peak observed after implantation is indicative of increased poly-crystallinity or nonuniform strain induced in the film. Annealing at 700°C led to a fairly sharp and intense diffraction peak and annealing at 900°C led to a further increase in the intensity of the peak, indicating an improvement in the crystalline quality of the film and the restoration of the predominantly \(\{110\}\) texture of the film.

**Discussion**

As seen in the cross-sectional SEM image of Fig. 5, the deposited Mo film has a columnar or fibrous morphology. XRD confirms the predominantly \(\{110\}\) texture of \([110]\) planes parallel to the surface of this film. The various crystallographic planes of body-centered cubic (bcc) Mo crystals have vacuum work functions ranging from 4.3 to 4.95 eV.\(^7\) The \(\{110\}\) Mo surfaces are the most densely packed in the bcc system and possess the highest work functions. The columnar microstructure is thus crucial in obtaining the high work functions (~5 eV) observed from the unimplanted samples. The work function lowering observed after 700°C annealing and the subsequent increase in the work function after 900°C annealing can be attributed to competing chemical changes (nitrogen segregation) and structural changes (improvement of crystalline quality) in the film between these temperatures. The segregation of nitrogen at the interface leads to an initial lowering of the work function (annealing at temperatures up to 700°C). While increasing the annealing temperature does increase the nitrogen concentration at the interface, it also leads to an improvement in the crystalline quality of the film and presumably increases the contribution of the \(\{110\}\) Mo planes to the work function. Thus, the subsequent increase in the work function...
tion is observed to be dependent on the implant dose and energy and the resulting crystalline damage induced by the implant. An optimization of the implant dose and energy will hence be necessary to control the final work function.

Metal work functions at dielectric interfaces have been observed to be dependent on the permittivity of the dielectric. While the interfacial Mo work function does vary with the dielectric being used, the variation is within 200 mV of the vacuum surface work function of the (110) crystallographic planes of Mo (4.95 eV). This observation indicates the applicability of Mo as a bulk-Si PMOS gate electrode. Selective nitrogen implantation into the Mo film is a relatively straightforward technique to modulate the Mo work function over the range of the Si energy bandgap, so that Mo is an attractive candidate gate electrode material for bulk-Si CMOS devices and also for ultrathin body SOI-CMOS devices.

Conclusions

The effect of nitrogen implantation and thermal annealing on the work function of Mo gate electrodes is presented. Nitrogen is observed to segregate at the Mo/SiO₂ interface upon thermal annealing, lowering the interfacial Mo work function from a relatively high value of ~5 eV. The ability to tailor the Mo work function over a fairly wide range makes it an attractive candidate for future CMOS technology generations.

References