

Study of diffusivity and electrical properties of Zr and Hf in silicon

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Downscaling of the size of transistors and gate dielectric thickness has reached the practical limit of ~ 1.2 nm of SiO₂ thickness, beyond which new materials are required to achieve the desired device performance. A large variety of high-k dielectric materials have been suggested to replace silicon dioxide. Some of them, such as TiO₂, Ta₂O₅, SrTiO₃ appear to not be thermally stable on silicon, and a thin barrier layer is required to prevent reaction and interdiffusion at the interface. In contrast, such materials as ZrO₂, ZrSiO₄, HfO₂, HfSiO₄, Al₂O₃, Y₂O₃, as well as Y and Hf silicates showed better stability on bare silicon. Since penetration of even very small amounts of these metals into the device area can potentially be detrimental to the device performance or even cause a device failure, it is important to characterize the electrical properties and diffusivity of the elements contained in these high-k dielectrics in silicon.

In this paper we report experimental studies of diffusivity and electrical properties of Zr and Hf in silicon. Zirconium and Hafnium were either implanted with the energies of 70 keV or 1.8 MeV, or sputtered on the sample surface. The samples were subsequently annealed in the temperature range from 700⁰C to 1200⁰C for 3-90 hours in argon. The diffusion profiles were characterized by secondary ion mass spectrometry (SIMS) and spreading resistance. Electrical properties of metals were assessed by a variety of capacitance techniques, including Deep Level Transient Spectroscopy and Thermally Stimulated Capacitance, and by photoluminescence.

SIMS measurements of implanted and annealed samples revealed very weak spreading of the implantation profiles of Zr and Hf after high temperature anneals. The diffusion coefficients extracted from fitting the profiles before and after the diffusion anneal were (1-3)×10⁻¹⁵ cm²/s at 1000⁰C and (3-10)×10⁻¹⁴ cm²/s at 1100⁰C for Hf and 5×10⁻¹⁵ cm²/s at 1100⁰C for Zr. Annealing of surface-sputtered samples followed by the spreading resistance analysis revealed a change of the electrical properties of the substrate to the depth of 10-15 microns from the surface after a 20-60 h anneal at 900-1200⁰C in argon. The concentration of the electrically active species detected in the spreading resistance profiles did not exceed 10¹⁵ cm⁻³, i.e., was below the detection limit of SIMS. The diffusivities of the mobile species, as determined from the spreading resistance profiles, was approximately 10⁻¹² cm²/s for Hf and 2×10⁻¹² cm²/s for Zr at 1100⁰C. A possible explanation of this phenomenon is

that both Zr and Hf diffuse via substitutional and interstitial (mobile) sites. The diffusivity of the interstitial species is several orders of magnitude higher than that of the substitutional species, but their solubility does not exceed (2-3)×10¹⁵ cm⁻³ at 1100⁰C. Therefore, the fast diffusing interstitial components of Zr and Hf cannot be detected by SIMS.

Using deep level transient spectroscopy (DLTS), it was found that Zr and Hf introduce deep level defects in the upper and lower half of the silicon band gap, some of which were in a good agreement with the Lemke's data [H.Lemke, Phys. Stat. Sol. (a) **122**, 617 (1990)]. Spreading resistance analysis of surface-diffused samples revealed strong acceptor activity of both Zr and Hf.

Photoluminescence analysis of a sample which was implanted with Hf at 80 keV and annealed for 3 h at 1000⁰C in argon revealed several strong lines in the spectral region between 1.3 μm and 1.6 μm. These lines were very strong at the temperature of approximately 12 K, remained visible up to the temperature of 70 K, but disappeared completely as the sample was heated to room temperature. This photoluminescence signal was not observed on 1.8 MeV implanted or surface-sputtered samples. The PL data on Zr implanted/diffused samples were ambiguous.