High Temperature Oxidation of Nickel Silicides Films Formed from Thin Ni Films

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Transition metal silicides (NiSi, TiSi2, CoSi2, etc) are widely used in the semiconductor industry, e.g. complementary metal-oxidesemiconductor (CMOS) devices, as ohmic contact, gate electrodes, diffusion barriers and local interconnects. Nickel silicides are one of the most widely studied silicide systems due to their high temperature performance and micro/nanoelectronics application.

In this work the phase formation and thermal oxidation stability of NiSi and NiSi2 thin films on n-type Si (111) substrates have been investigated. The objects to study were thin-film layers of Ni (200nm) on crystalline Si substrate of orientation (111) doped with phosphorus. Thin-film system Ni/Si obtained by electron-beam deposition in vacuum $2{\cdot}10^{-4}$ Pa. After deposition the samples were annealed in a furnace with oil-free vacuum pumping $1.33{\cdot}10^{-3}$ Pa in the temperature range 470 – 1270 K.

As-deposited and annealed films were examined with an EMR-100 electron diffraction unit. The calculated values of interplanar spacing were compared with the corresponding tabulated values. The thermogravimetric analysis was carried out with a "Derivatograph Q-1500D" unit in the following conditions: temperatures range 300–1270 K, sample weight ~ 20mg, open air, heating rate 10 K/min.

In the initial state, the Ni (200 nm)/Si thin-film system with a layer of "natural" oxide SiO_2 (~ 6–10 nm) was present nickel phase. At annealing temperature 770 K a number of nickel phase remains after annealing the system. Further increase in annealing temperature to 970 K leads to formation of Ni_2Si and NiSi. Remaining phase of nickel is not observed. Nickel disilicide formed at temperature of 1270 K.

According to data TGA, high-temperature oxidation of the NiSi films and the associated increase in weight begins at about 250 degree higher than the oxidation of a silicon substrate. The oxidation of NiSi film starts at 930 K, which is approximately 100 K below the temperature at which $NISi_2$ films start oxidising. For both NiSi and $NISi_2$ oxidation types the SiO_2 thin protective layers have been formed. When temperature increases, the mass increment NiSi films becomes greater than that of $NiSi_2$ films. This difference is three times as great at 1270 K, which is due to the difference in their structure and stoichiometry. Due to high silicon content, nickel dicsilicide forms dense layers of silica on the surface during oxidation, which has substantial impact on the oxidation rate.