Functional Materials 16, No.4 (2009) © 2009 — STC "Institute for Single Crystals"

Multilayer film heterostructures. Silicides

S.I.Sidorenko, Yu.N.Makogon, E.P.Pavlova, S.M Voloshko

National Technical University of Ukraine "KPI", Kyiv, Ukraine

Received September 15, 2009

The formation of heterostructures based on nanoscale silicide films in limiting states are exemplified. The nanoscale silicide films of a required phase composition are shown to be obtainable by formation of specific zones, different type interlayers referred to as the diffusion-controlling layers between the metal layer and substrate (silicon single crystal).

Показаны примеры получения гетероструктур на основе наноразмерных силицидных пленок в предельных состояниях. Показано, что получение наноразмерных силицидных пленок необходимого фазового состава обеспечивается формированием между слоем металла и подложкой (монокристаллом кремния) особенных зон, прослоек разного типа — диффузионно-контролирующих слоев.

A special interest in silicide films is connected with the wide variation range of their properties from those typical of metals to semiconductor ones as well as with enhanced thermal and chemical resistance as compared to metals [1, 2]. In traditional MOS (metal-oxide-semiconductor)-silicon technology, the silicide films are used as functional elements intended for different purposes (rectifying Schottky diodes, ohmic contacts, gate electrodes, emitters and interconnections).

Among epitaxial films which can be formed on single-crystal silicon plate, of a particular interest are disilicide $CoSi_2$ with metal conductivity and low specific resistance (about 15 $\mu\Omega\cdot$cm) and semiconductor silicide Mn_4Si_7 which due to its unique electrical and optical properties (thermal emf anisotropy with coefficient exceeding 150 μV/K as well as direct band gap of 0.68–0.83 eV thickness) is a new material of good promise for use in thermoelectric devices and in development of high-temperature generators and sensors [3].

The lattice mismatch for $CoSi_2$ and Si substrate makes about 1.2 % at room temperature, thus enabling its epitaxial growth. However, in a single-layer Co/Si film composition, $CoSi_2$ layer grows as a polycrystal due to high rate of solid-state Co and Si interaction reactions. In this work, the problem of $CoSi_2$ epitaxial film formation was solved by creation of a specific layer, a diffusion-controlling membrane (DCM) of intermediate nanodimensional Ti and SiO_2 layers between the Co film and Si substrate. The controlling role of DCM was to decelerate the diffusion flows of Co and Si atoms into the solid-state reaction zone and to provide the $CoSi_2$ epitaxial growth. Under annealing of the film compositions under investigation, the diffusion processes are accompanied by deterioration of SiO_2 layer and formation of Co–Ti–Si ternary compound which was identified in this work as Co_3Ti_2Si phase. The thickness values of initial Ti and SiO_2 layers were selected to provide the ternary compound layer of about 10 nm thickness [4]. The decomposition of ternary compound at higher annealing temperatures results in transfer of Co atoms to Si substrate and formation of $CoSi_2$ epitaxial film. Calculation of effective diffusion coefficient of Co atoms has shown that it was decreased by 3 orders [5], (Fig. 1). The electric resistance under annealings is varied corresponding to a curve with a maximum. The lowest resistance (about 15 μm·cm) corresponds to formation of $CoSi_2$. It is established that the

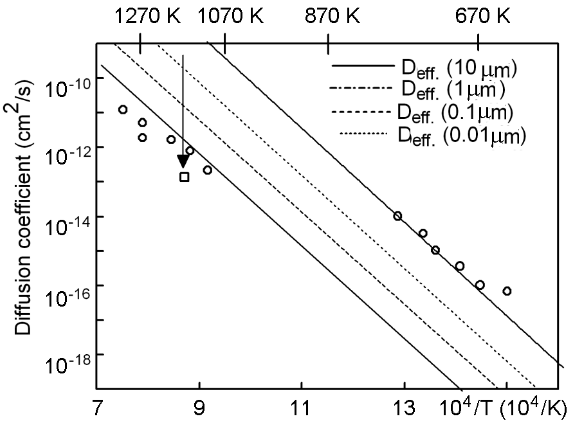

Fig. 1. Comparison of experimentally determined effective diffusion coefficient of Co (point □) with literature data [5].

$CoSi_2$ epitaxial layer is formed in a sample with Ti layer of 4.7 nm and SiO_2 layer of 1.91 nm after annealing in ultrahigh vacuum at 1170 K during 30 s. Its thickness is 70 nm and the epitaxial correlations with the silicon substrate were established to be (001)[100]$CoSi_2$||(001)[100]Si. $CoSi_2$ is thermally stabile up to 1320 K.

The lattice mismatch for Mn_4Si_7 and Si makes about 1.8 %, thus, its epitaxial growth on a silicon single crystal is possible, too. However, formation of Mn_4Si_7 by solid-state reaction during annealing or by Mn reactive deposition onto heated substrate is accompanied by formation of silicide film of polycrystalline structure due to high rate of solid-state reactions in the Mn/Si film system. To lower the chemical activity of substrate surface, a buffer silicon layer of 100 nm is deposited thereon under ultra high vacuum. The influence of substrate temperature on the structure and morphology of Mn_4Si_7 silicide forming at deposition of nanodimensional Mn film was studied. It was established that at $T_{subst.} < 820$ K, the continuous but polycrystalline silicide layer is formed. At $T_{subst.} > 820$ K, the film consists of separate epitaxial grains of Mn_4Si_7 and is incontinuous.

To form the epitaxial layers of Mn_4Si_7 on silicon, it is used the approach basing on the change in growth kinetics of silicide film due to use of Sb surfactant, a specific layer between the metal film and substrate. The surfactant decreases the substrate surface activity and produces its wetting. The Sb layer was deposited previously onto silicon surface at 870 K. The subsequent reactive deposition of Mn film is accompanied by Mn_4Si_7 formation.

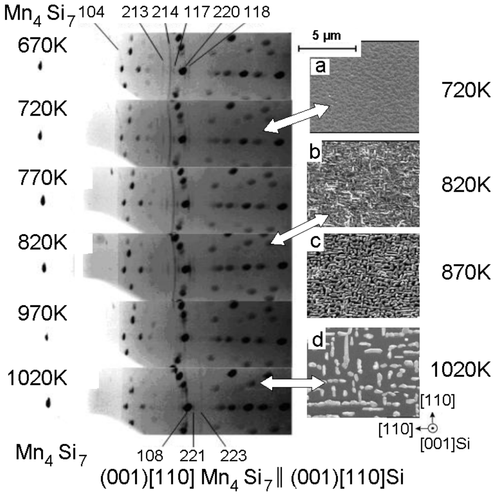

Fig. 2. Effect of substrate temperature on the structure and morphology of Mn_4Si_7 film in Mn(20 nm)/Si(100 nm)/Si(001) structure.

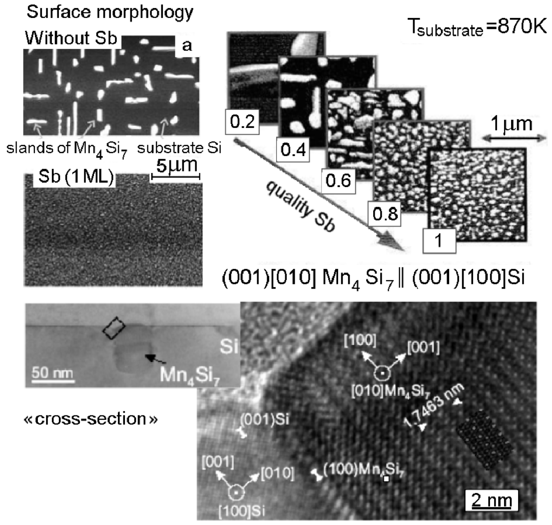

Fig. 3. Effect of Sb surfactant on the structure and morphology of Mn_4Si_7 film.

It has been established that an increase of surfactant layer thickness influences the morphology of Mn_4Si_7 film and produces an increase of the area occupied by silicide (Fig. 3). At surfactant layer thickness of 1 monolayer, the formation of large grains is suppressed and density of small grains which inherit the substrate orientation is increased [6–8]. The calculations have shown that the surface diffusion coefficient of Mn atoms is decreased by 6 orders, thus resulting in suppression of large silicide grains growth. The cross-section examination of the film sample by TEM show that in the absence of surfactant, the silicide grains grow on the substrate surface and when the surfactant is present, those grow into substrate and film with smooth surface morphology is formed.

Thus, the introduction of nanoscale Ti and SiO_2 layers as diffusion controlling layer (DCL) into the Co/Si film composition provides a controlled growth of $CoSi_2$ epitaxial film on silicon single crystal by deceleration of the diffusion processes due to formation of the Co_3Ti_2Si intermediate phase that reduces the effective diffusion coefficient of Co atoms to the solid-phase reaction zone and provides the formation of epitaxial $CoSi_2$ disilicide. The controlled growth of epitaxial Mn_4Si_7 silicide layers on the single-crystalline silicon of (001) orientation is provided by introduction of a ultra-thin surfactant layer as a DCL between the Mn film and Si substrate, thus providing a change in the film growth kinetics. The surfactant monolayer introduction cdauses a reduction in the surface diffusion coefficient of Mn atoms on Si(001), thus providing the layer-by-layer growth mechanism oriented film of a film consisting of small Mn_4Si_7 grains inhering the substrate orientation and formation of an epitaxial Mn_4Si_7 silicide layer.

References

1. S.I.Sidorenko. Inorganic Meterials Science: An Encyclopedial Issue. Vol. 1. Naukova Dumka, Kyiv (2008) [in Russian].
2. S.I.Sidorenko, Yu.N.Makagon. Actual Problems of Modern Materials Science. Vol. 2. Akademperiodika, Kyiv (2008) [in Russian].
3. K.Maex, M. Van Rossum. Properties of Metal Silicides, INSPEC, London (1995).
4. Yu.N.Makagon, S.M.Voloshko, E.P.Pavlova, et al., *Metallofiz. Noveysh. Tekhnol.* **23**, 1455 (2001).
5. T.Barge, P.Gas, F.M.D'Heurle *J. Mater. Res.*, 10, 1134 (1995).
6. Yu.N.Makagon, E.P.Pavlova, S.I.Sidorenko, et al., *Metallofiz. Noveysh. Tekhnol.* **24**, 1455 (2002).
7. Yu.N.Makagon, S.I. Sidorenko, G. Beddies, et al., in: 2nd Intern. Conf. Surface, Coating and Nanostructured Materials (NanoSMat) 2007, Portugal, 2007, Abstract Book, P.142
8. Yu.N.Makagon, S.I. Sidorenko, A.V.Mogilatenko, *Metallofiz. Noveysh. Tekhnol.* **30**, 1383 (2008).

Багатошарові плівкові гетероструктури. Силіциди

С.І.Сидоренко, Ю.Н.Макогон, Е.П.Павлова, С.М.Волошко

Подано приклади отримання гетероструктур на основі нанорозмірних силіцидних плівок у граничних станах. Показано, що отримання нанорозмірних силіцидних плівок необхідного фазового складу забезпечується формуванням між шаром металу і підкладкою (монокристалом кремнію) особливих зон, прошарків різного типу — дифузійно-контролюючих шарів.