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Monocrystalline molybdenum silicide based quantum dot superlattices grown by chemical vapor deposition

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ABSTRACT

This paper presents the growth of doped monocrystalline molybdenum-silicide-based quantum dot superlattices (QDSL). This is the first time that such nanostructured materials integrating molybdenum silicide nanodots have been grown. QDSL are grown by reduced pressure chemical vapor deposition (RPCVD). We present here their crystallographic structures and chemical properties, as well as the influence of the nanostructuration on their thermal and electrical properties. Particularly, it will be shown some specific characteristics for these QDSL, such as a localization of nanodots between the layers, unlike other silicide based QDSL, an accumulation of doping atoms near the nanodots, and a strong decrease of the thermal conductivity obtained thanks to the nanostructuration.

1. Introduction

The nanostructuration of thin films has considerably improved for many years. Nowadays, thin films nanostructuration, such as superlattices, nanowires or quantum dots superlattices, can be found for many materials, especially in silicon and germanium alloys. Si and SiGe alloys are base materials in microelectronic field. The improvement of their electrical, optical or thermal properties thanks to the nanostructuration make them very interesting materials in many applications such as transistors [1,2], optoelectronic devices [3,4], solar cells [5,6] or thermoelectrics [7–9].

Some studies have already shown the influence of the integration of nanodots on the decrease of the thermal conductivity: iron-silicide-based nanodots at the surface level [10], nanostructured silicon integrating Si nanocrystals [11] or QDSL including Ge-based nanodots [12–15].

In this paper, we present the first growth of thin films QDSL based on molybdenum silicide nanodots inside a n-doped SiGe monocrystalline matrix. The choice to grow such nanomaterials has been recently proposed in literature. Indeed the authors have theoretically shown that such nanostructured materials had lower thermal conductivity than their bulk references [16]. QDSL integrating titanium silicide nanodots have also already been grown recently [17,18]. In these papers, the influence of nanostructuration on thermal properties has been underlined. But, in Ref. [16], authors have shown that the nature of metallic

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silicide can influence largely the thermal properties, and more precisely, that molybdenum silicide nanodots should allow a larger decrease of thermal conductivity compared to previous titanium silicide nanodots in QDSL.

2. Experimental details

Monocrystalline samples are epitaxially grown onto lightly doped SOI wafers in a modified Epi-Centura Reduced Pressure CVD industrial cluster tool built by Applied Materials. This technique has already been used for successfully growing nanostructured silicon-based thin films [7,14,15,17,18]. The precursor chosen for the Mo-based QD growth is molybdenum pentachloride ($MoCl_5$), which is solid at ambient temperature. A specific, adapted apparatus allowing the controlled recovery of the precursor vapor was built and coupled to the Centura tool. This apparatus has a temperature and pressure control system, and H_2 is employed as the carrier gas to send the gaseous portion of the precursor to the reaction chamber. The SiGe layers are grown in the same chamber using silane (SiH_4) and germane (GeH_4) gas as precursors. The samples were doped in situ using phosphine (PH_3) gas (n-type). The Ge content of SiGe layers inside the QDSL is set to around 10%.

The flow rate values of $MoCl_5$, SiH_4, GeH_4, PH_3 and H_2 are 85 sccm, 85 sccm, 15 sccm, 20 sccm and 20 SLM, respectively. The SiGe growth rate is 3 nm/s.

Deposition temperature and pressure are 800 °C and 10 Torr respectively. The total thickness of QDSL is 1.25 µm, corresponding to 25 alternations between QD and 50 nm SiGe layers. A 200 nm SiGe buffer layer is deposited before the QDSL. This buffer layer allows to reduce dislocations due to the lattice mismatch between the SiGe thin films and the Si substrate, to lower the interdiffusion between the Ge atoms from the QDSL and the Si atoms from the substrate, and to maintain a constant Ge content trough in all SiGe layers of the QDSL. QDSL are then obtained by alternating SiGe layers (using SiH_4 and GeH_4) and QD layers ($MoCl_5$ only). The silicidation of molybdenum is performed directly during the QD deposition.

3. QDSL structural properties

The QDSL structure is analyzed by Transmission Electronic Microcopy (TEM). These TEM analyses are performed at 200 kV, including High-Angle Annular Dark Field (HAADF) images in the scanning mode (STEM), which allow us to acquire both high-resolution images and chemical mapping using the Energy-Dispersive X-ray Spectroscopy (EDS) technique. The samples are prepared using a tripod polishing technique. Fig. 1 presents global cross-plane views of the n-type monocrystalline QDSL, showing the 25 alternations, and which permits particularly to measure the QD diameters d and each SiGe layer's thickness e. By analyzing the images and statistically calculating the mean QD diameters and layers thickness, values of d = 5 nm and e = 50 nm are obtained.

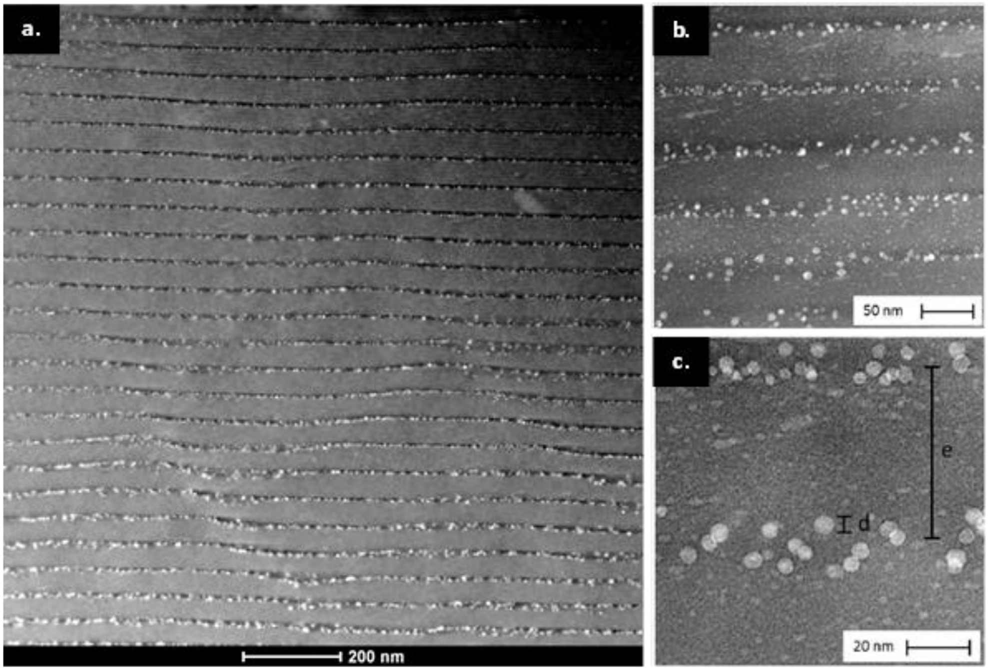

Fig. 1. Cross-section STEM/HAADF images of n-type monocrystalline QDSL: a) global view showing the 25 alternations, b) global view showing the Mo-based nanodots layers, c) higher magnification of the image showing a QD diameter of d = 5 nm and a layer thickness e = 50 nm.