Effects of Lattice Defects on Electronic Structure and Optical Properties of Higher Manganese Silicide Mn_4Si_7 and $Mn_{17}Si_{30}$ Thin Films

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Higher manganese silicides (HMSs) are attractive materials that can be utilised for thermoelectric [1] and photovoltaic power generation, light emittance and detection [2]. In spite of a great number of works on HMS synthesis and investigation of their physical properties, both in bulk and 1D and 2D nanostructure forms, several technological and scientifically important issues remain not fully explored. The HMS family includes several homologous phases with Nowotny chimney ladder (NCL) tetragonal crystal structure that is composed of tetragonal manganese ß-Sn-like chimney subcell and double-helically arranged silicon subcell. Five different commensurate HMS compounds in chemical composition range $MnSi_{1.72\text{-}1.75}$, which are $Mn_{11}Si_{19}$ ($MnSi_{1.727}$), $Mn_{15}Si_{26}$ ($MnSi_{1.733}$), $Mn_{26}Si_{45}$ ($MnSi_{1.730}$), $Mn_{27}Si_{47}$ ($MnSi_{1.741}$) and Mn_4Si_7 ($MnSi_{1.75}$), have been reported with the atomic position determined by X-ray diffraction (XRD) on bulk samples [3]. Along with these well–known HMS phases other HMS compounds such as Mn_7Si_{12} ($MnSi_{1.714}$), $Mn_{26}Si_{45}$ ($MnSi_{1.731}$), $Mn_{19}Si_{33}$ ($MnSi_{1.737}$), and $Mn_{39}Si_{68}$ ($MnSi_{1.744}$) have been described in XRD and electron diffraction studies on nanosized samples, thin films, nanowires, nanorods [4]. Nevertheless, the list of possible homologous HMS phases may be not fully determined because there is evidence of existing other NCL commensurate phases in other systems and incommensurate HMS phases. This variety of the homologous HMS phases, where Si content varies only in the range of 63-64 at. %, gives rise to the uncertainty in the transport and optical properties experimental studies of these materials.

Here we present a study on electronic structure, optical and transport properties of two HMS phases, well-known Mn_4Si_7 and rarely reported $Mn_{17}Si_{30}$ thin films grown on Si(001). N-type degeneracy was shown theoretically for $Mn_{17}Si_{30}$ compound whereas Mn_4Si_7 is non-degenerate p-type semiconductor. This fills a gap in theoretical explanations of n-type conductivity for HMS phases observed earlier experimentally [5]. Degeneracy is confirmed by both absorption coefficient measurements beyond the band gap energy (Fig. 1b) and resistivity measurements. Temperature dependence of the resistivity has a metallic character whereas Mn_4Si_7 shows typical behaviour for non generated semiconductor which corresponds to literature data. Moreover, an effect of silicon and manganese vacancies and silicon spirals shifts on electronic structures and optical properties were examined by ab initio calculations. It is asserted that such defects can results in degeneracy, change of Fermi level position, 100 % spin polarisation and magnetic moment appearance. This explains also some findings we observed on magnetic and optical experimental data.

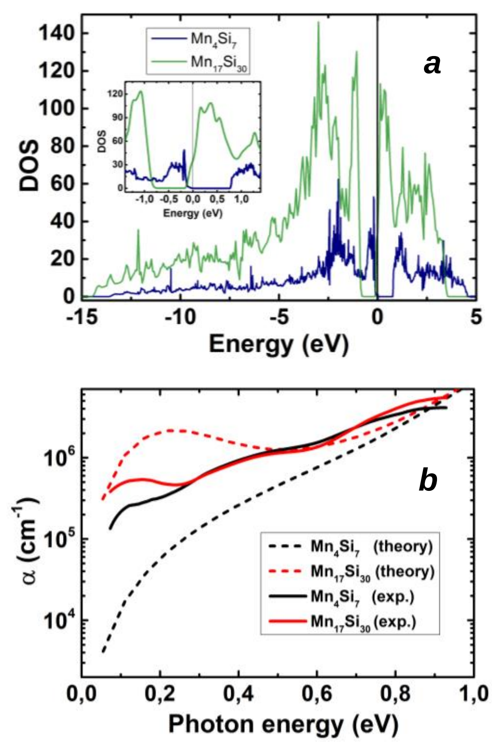

Fig. 1 (a) Density of electronic states for Mn_4Si_7 and $Mn_{17}Si_{30}$ compounds. (b) Theoretical and experimental spectra of absorption coefficient α for Mn_4Si_7 and $Mn_{17}Si_{30}$ compounds.

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