INVESTIGATIONS OF METAL-SEMICONDUCTOR THIN FILMS AND NANOSTRUCTURES OF LAYERED MATERIALS

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ABSTRACT

Semiconductor-metal (MS) heterostructures or heterojunctions are the foundation of modern electronic as well as optoelectronic devices. The most important characteristic when a metal is overgrown on a semiconductor substrate is the formation of the MS junction manifested by the work function difference of the metal and the semiconductor in the form of a potential barrier. This potential barrier is of central importance in determining the performance of various devices. However, engineering the MS contact and to make a sharp MS interface or junction to achieve the required device performance is not an easy job. In most cases, interdiffusion of atoms around the MS junction occurs during the growth process which results in deteriorating device performances. This shortcoming of MS interface can be controlled to some extent by placing an insulating material in between metal and semiconductor electrodes where diffusion and growth kinetics could be taken care of due to the presence of the insulating layer. As a result, metal-insulator-semiconductor (MIS) systems have got a huge attention which could demonstrate better device characteristics depending on the requirements. However, the most used dielectric like SiO_2 on Si substrate has interface states and defects which could be responsible for the diffusion kinetics to take place even on a MIS system. This makes the investigations related to the growth, diffusion kinetics, formation of new interface governed by growth parameters, defects and interstitial processes essential to understand the reliability of the device performance. Thus, a detailed study of growth and interface formation of MIS systems is of great importance.

A strain-induced growth of copper (Cu) and its interaction on a thermally grown, 270 nm thick SiO_2 layer on Si(111) substrates have been investigated. The Cu deposition at 600^0C for 30s followed by post deposition annealing initiates the growth of triangular nanocrystallites on the surface via void filling mechanism even on a 270 nm thick SiO_2 layer. Substrate temperature seems to play a key role in the island formation via diffusion and segregation mostly through void-filling process where 3 fold crystal symmetry of the Cu as well

as of the substrate gets reflected on the morphology of the island growth. Our experimental investigations validate the formation of Cu-oxides, Cu-silicides and an intermediated Cu-O-Si phase in the grown film.

Over the past years, the increased demand for miniaturisation of devices has led to the incorporation of nanostructured materials and two dimensional (2D) layered materials into semiconductor devices. The successful isolation of graphene, a single layer of carbon atoms arranged in a hexagonal motif, from graphite is a breakthrough discovery leading to a different area of research called 2D materials. Transition metal dichalcogenides (TMDs) like MoS_2, WS_2 etc. with a thickness dependent indirect to direct bandgap crossover come under the 2D van der Waals (vdWs) materials which have received enormous attention recently. These materials possess novel electronic, optical, optoelectronic, catalytic properties, many of which could be considered superior to graphene whose technological applications are somewhat limited by its zero band gap nature at the K points.

Nanostructures of TMDs can be easily synthesized and incorporated into semiconductor devices for various applications. We have synthesised MoS_2 nanostructures by a simple liquid phase exfoliation (LPE) of MoS_2 powder in organic solvents followed by microwave treatment (MW) for 10 mins (S1). The probe sonication and the MW treatment play an important role in rolling and curling of the MoS_2 nanosheets to give rise to MoS_2 spheres and rod/tube like-structures with diameter approximately 150–200 nm. The MoS_2 nanorods formed in this fashion are hollow inside with a wall thickness of 15–20 nm and the length of the nanorods is found in the order of several micrometers. The MoS_2 nanostructures, thus, obtained are mainly comprised of 2H semiconducting phase and exhibit good emission.

By simply changing the MW treatment time to 30 mins (S2), we observe that the nanostructures of rods/tubes, spheres and the sheets formed in the sample consists of a mixture of metallic 1T and semiconducting 2H phases with more of 1T than of 2H with a ratio of 70 (1T): 30 (2H). This nanostructured sample S2 also exhibits high emission yield, however, less compared to the 10 min MW irradiated sample, S1 due to the presence of more metallic 1T phase. The estimated width/diameter of the nanostructures in this case is in the range of 50-150 nm. High resolution transmission electron microscope (HRTEM) investigations performed on S2, clearly demonstrate the formation of sharp coplanar heterojunction of hybridized 1T-2H superlattice phase. This kind of coplanar heterojunctions composed of same layered material with different structural polymorphs have drawn immense interest recently due to low contact resistance and high carrier injection rate owing to low Schottky barrier height. Present research has largely focused on efficient exfoliation of these layered materials and their restacking to achieve better performances. HRTEM investigations reveal evidence of surface ripplocations within the same exfoliated layer of MoS_2. The structural stability of 1T-2H superlattice phase during HRTEM measurements under an electron beam of energy 300 keV is studied. We find that while the nanostructures comprised mainly of 2H semiconducting phase (S1) are very vulnerable towards 200 - 300 keV electron beam, the exfoliated sheets constituted of 1T-2H hybridized phase exhibit no sign of electron beam interaction. This structural stability could be either associated to the change in electronic configuration due to induction of the restacked hybridized phase with 1T- and 2H- regions or to the formation of the surface ripplocations. Surface ripplocations can act as an additional source of scattering centers to the electron beam and also it is possible that a pulse train of propagating ripplocations can sweep out the defects via interaction from specific areas of MoS_2 sheets.

In this thesis, we first study the growth kinetics and interface formation for a conventional MIS system of Cu-SiO_2/Si. Even on a thick SiO_2 dielectric layer of 270 nm, we observe atomic diffusion forming different phases of Cu-oxides, Cu-silicides and an intermediate phase of Cu-O-Si in the sample. Evidence of triangular voids on the surface and the formation of triangular nanocrystallites clearly demonstrate that the formation of islands has taken place via void filling mechanism even on a thick SiO_2 layer. Then we have focussed our studies on to a more recent semiconducting layered material of MoS_2 and tried to develop a simple top-down strategy to exfoliate MoS_2 nanostructures which could have potential technological applications. We have taken a MW assisted easy, fast and efficient route to induce high concentration of metallic 1T phase in the original 2H matrix of exfoliated MoS_2 layers. This mixed phase demonstrates high structural stability under 200 – 300 keV electron beam and shows a sharp MS junction. This structure could be considered superior to the conventional MS interface due to the lack of lattice mismatch and subsequent reduction of strain in the structure.