Applied Surface Science 428 (2018) 623–629

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Full Length Article

Fabrication of $NiSe_2$ by direct selenylation of a nickel surface

Haoliang Sun[a,b,c], Zhaofeng Liang[a], Kongchao Shen[a,d], Mi Luo[a], Jinbang Hu[a], Han Huang[e], Zhiyuan Zhu[a,b], Zhijun Li[a], Zheng Jiang[a,b], Fei Song[a,b,*]

[a] Shanghai Synchrotron Radiation Facility and Shanghai Institute of Applied Physics, Chinese Academy of Sciences, 201204, China
[b] Key Laboratory of Interfacial Physics and Technology, Chinese Academy of Sciences, 201204, China
[c] University of Chinese Academy of Sciences, Beijing, 100100, China
[d] Department of Physics, Zhejiang University, 310027, Hangzhou, China
[e] School of physics and electronics, Central South University, Changsha, 410083, China

ARTICLE INFO

Article history:
Received 24 May 2017
Received in revised form 5 September 2017
Accepted 24 September 2017
Available online 25 September 2017

Keywords:
TMD
Epitaxial growth
Direct selenylation
Nickel diselenide
PES

ABSTRACT

The emergence of transition metal dichalcogenides (TMD) as an exciting class of materials with appealing potentials in electronic and optoelectronics has drawn intensive attention in the past few years. Herein, we report the fabrication of $NiSe_2$, which has been predicted to be a promising candidate in the field of electrocatalyst, by direct selenylation of the nickel substrate after epitaxial growth of selenium on a nickel foil. With a combination of photoelectron spectroscopy (PES), X-ray diffraction (XRD), scanning electron microscopy (SEM) and density function theory (DFT) calculations, it is possible to identify the phase transition among the previously reported stable Ni-Se phases and the ultimate formation of $NiSe_2$ species by external annealing at varying temperatures. While SEM reveals the morphology of $NiSe_2$ film with flat terraces, XRD, XPS and DFT calculations demonstrate that $NiSe_2$ is the relatively stable phase formed on the Ni substrate from the cohesive energy point of view. Furthermore, valence band spectra point out the nonmetallic level of these different Ni-Se compounds, agreeing well with literature reports. In the end, our report may indicate a feasible approach to synthesize the pure NiSe2 species under solution-free condition and an encouraging step forward towards non-noble electrocatalysts.

1. Introduction

Transition metal dichalcogenide (TMD) have attracted tremendous interests recently as the basis for the appealing generation of transistors and optoelectronic devices, based on their tunable electronic properties with layered structures [1–4]. In practice, there have been considerable efforts devoted to the fabrication of varying forms of TMD materials with precisely controlled chemical compositions, physical dimension and sizes, or heterostructure interfaces [5]. Specifically, transitional metal diselenide (MSe_2, M = Ni, Co, Fe) turns to be one sort of the mostly investigated TMDs, due to its intriguing electronic, optical, and chemical properties [6–9]. For instance, previous reports have demonstrated that nickel diselenide ($NiSe_2$) is an efficient electrocatalyst acting as the counter electrode (CE) for dye-sensitized solar cells (DSSCs) and an attractive non-noble-metal catalyst for electrochemical catalysis such as water splitting [10–13]. Although platinum and other noble-metal materials have been proven to be the most active catalyst, they suffer from scarcity and high cost, seriously limiting their widespread application in industry. While nickel is relatively abundant in nature, $NiSe_2$ therefore presents appealing potentials for industrial application in the future.

Because of the valence electronic configuration of Ni ($3d^8 4s^2$), its valence state ranges from 2^+ to 4^+ [14]. In addition, due to the small difference in electronegativity between Ni (c = 1.8) and Se (c = 2.4), they can form a variety of nickel selenides [15,16]. In fact, several stable phases have been reported at room temperature (RT): $NiSe_2$, NiSe, and Ni_3Se_2. The coexistence of different Ni-Se compounds make it rather difficult to get pure $NiSe_2$, as discovered from previous studies [17,18]. Consequently, feasible fabrication and integration of $NiSe_2$ becomes to be a practical topic. Nevertheless, efforts have been devoted to synthesizing the high-quality $NiSe_2$ material in the past decade [19,20]. Usually, a fixed molar ratio of 1:2 between nickel and selenium is used for the preparation of $NiSe_2$, as used in the hydrothermal synthesis, solvothermal route, electrodeposition method, solution chemical process and solid state synthesis [11,21–26]. However, these approaches with fixed molar ratio still cannot guarantee the formation of the pure $NiSe_2$ species, and inevitably bring in other Ni-Se compounds.

* Corresponding author at: Shanghai Synchrotron Radiation Facility and Shanghai Institute of Applied Physics, Chinese Academy of Sciences, 201204, China.
E-mail address: songfei@sinap.ac.cn (F. Song).

https://doi.org/10.1016/j.apsusc.2017.09.201
0169-4332/

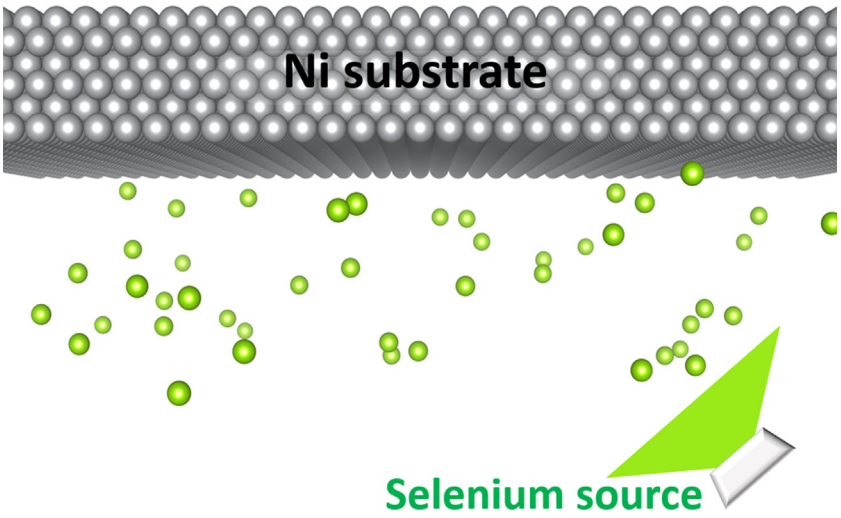

Fig. 1. Schematics for the epitaxial growth of Se films on a Ni substrate *via* thermal deposition.

Importantly, most of these routes take place in the solution environment and exposed to the atmosphere during the procedure, which brings the chance to get Ni or Se easily oxidized. To some extent, the oxidation of Ni or Se prevents the formation of single phase Ni-Se compound [27].

In this work, we present a convenient, controllable synthetic route to prepare $NiSe_2$ under solution-free condition, *via* on-surface selenylation of the nickel substrate in ultra-high vacuum (UHV) environment. In contrast to previous fabrication procedures, the proposed routine herein is totally straightforward: a single step by direct selenylation after epitaxial growth of the selenium film on a Ni surface [28,29]. With the help of on-surface selenylation after epitaxial growth under dry condition, it is expected that the pure Ni-Se species can be obtained. With a combination of various characterization techniques such as scanning electron microscopy (SEM), photoelectron spectroscopy (PES), X-ray diffraction (XRD) and density functional theory (DFT), we could identify the on-surface selenylation process of the Ni metal and the ultimate formation of $NiSe_2$ compound.

2. Materials and methods

2.1. Materials preparation

Nickle foil (99.994%, 0.1 mm thick) and selenium powder (99.999%) are both purchased form Alfa Aesar. Prior to the epitaxial growth of selenium, Ni foils (1cm × 1 cm) were first washed by HCl/H_2O (1:10) and triple rinsed by acetone and ethanol, and transferred afterwards into the ultrahigh vacuum chamber with a base pressure better than 5×10^{-10} mbar. After cycles of Ar^+ ion sputtering and thermal annealing at 773 K, the cleanliness was checked *in situ* by XPS and SEM. High-purity Se was thermally evaporated onto the Ni substrate after proper degas, while the Ni foil was kept at room temperature (RT) during the deposition. The thickness of selenium film was estimated from the XPS signal attenuation of the Ni $2p_{3/2}$ peak. In the current work, selenium film with a thickness of around 8 Å was prepared on the Ni foil, followed by thermal annealing to 373 K, 423 K, and 523 K for 30 min in UHV (as illustrated in Fig. 1). After *in situ* photoemission measurements, all the samples were also transferred to a separate SEM chamber for morphology characterization, as well as XRD measurement with synchrotron light.

For convincing comparison, a thick film of selenium (around 100 nm) was prepared on Ni substrate as a reference of the bulk chemical state for Se. Moreover, XPS core levels from a pure NiSe sample (99.9%, Alfa Aesar) were also recorded as reference.

2.2. Characterization techniques

In situ PES were performed in the UHV environment equipped with a monochromatic X-ray source (Al Kα: 1486.6 eV) and a Helium lamp (He I, hν= 21.2 eV), using a PHOIBOS 100 energy analyzer (SPECS) with the overall energy resolution around 0.05 eV. Photon energy was calibrated by comparing the binding energy of C1 s from a standard HOPG sample and the Fermi level of a clean Ni surface. Scanning electron microscopy (SEM, Zeiss merlin compact) was utilized to investigate the morphology of bare and selenizated nickel substrates. XRD was first characterized at the beamline BL14 B in Shanghai Synchrotron Radiation Facility (SSRF) with a wavelength of 0.6887 Å and a fixed incidence angle of 0.1°, and carried out again with a Cu Kα radiation (1.54 Å) at a fixed grazing angle of incidence 1° in the lab. In the end, DFT calculations were implemented to compare the stability of different Se-Ni compounds [30,31], which were performed using VASP code [32] with the gradient-corrected Perdew-Burke-Ernzerhof (PBE-GGA) exchange correlation functional [33]. In addition, the projector augmented wave (PAW) method was employed in the calculations [34], and the energy cutoff of the plane-wave basis sets was 500 eV.

3. Results and discussion

Fig. 2 presents the surface morphologies of the clean and selenium-covered Ni foil before and after annealing treatment. As mentioned previously, the sample covered with epitaxial Se film was annealed to 373 K and 423 K for 30 min, respectively. As seen in Fig. 2a from SEM image, the clean Ni foil is not as smooth as expected and tiny holes and scratches are discovered place by place, which might be related to the quality of nickel foil even after cycles of Ar^+ sputtering. Fig. 2b shows the surface morphology of the Ni substrate covered by Se film with the thickness around 8 Å. In contrast to the bare Ni surface, there is no more scratch presented, but instead, small clusters are identified with an average size about 40 nm (as marked with white dots in Fig. 2b) at a first glance. Actually, it makes sense for such observation since the epitaxial selenium film can easily cover the scratches, and the deposited selenium atoms would also prefer to accumulate around surface defects or step edges which induce the formation of nanoclusters [35], as revealed with white dots in Fig. 2b. Initial annealing to 373 K of the