

Materials science communication

## ZnO/aSi interface charge carriers transport in Li-ion secondary cell anodes



Joong Kee Lee\*, Aliaksandr A. Khodin

Center for Energy Convergence, Advanced Energy Materials Processing Lab, Korea Institute of Science and Technology, Hwarangno 14 gil 5, Seongbuk-gu, Seoul 136-791, Republic of Korea

### HIGHLIGHTS

- *n*-ZnO/*p*-aSi interface potential barrier controls electrons supply for Li coupling reaction.
- The interface electric field exceeds  $10^5$  V cm<sup>-1</sup> to draws in Li ions from ZnO into aSi.
- *n*-ZnO/*p*-aSi heterojunction could have ohmic or diode type behavior under initial charging.

### ARTICLE INFO

#### Article history:

Received 11 October 2012

Received in revised form

25 September 2013

Accepted 23 January 2014

#### Keywords:

Interfaces

Oxides

Semiconductors

Electrical conductivity

Electrochemical properties

Heterostructures

### ABSTRACT

Electron and Li-ion transport at the *n*-ZnO/*p*-aSi (amorphous Si) heterojunction interface is analyzed for the initial charging conditions of a secondary battery anode. The ohmic and diode-type current–voltage characteristics of the junction are investigated for varying doping levels of aSi and ZnO layers. The interface potential barrier impacts the electrons supply to control the  $\text{Li} + \text{ZnO} \rightarrow \text{Li}_2\text{O} + \text{Li}_x\text{Zn}$  reaction. The interface electric field could exceed  $\sim 10^5$  V cm<sup>-1</sup> and draws in Li ions from zinc oxide into the silicon layer. Relatively low-level doping ( $\sim 10^{18}$  cm<sup>-3</sup>) of the semiconductors is preferred for the optimum draw-in effect. During the initial charging, when the Li content in ZnO (as substitution  $\text{Li}_{\text{Zn}}$  acceptors) does not exceed the solubility level ( $\sim 10^{19}$  cm<sup>-3</sup>), the overall doping maintains the *n*-type, and the interface electric field continues to draw in Li ions towards silicon. Under further increase of Li content at interstitials, the layer conductivity is converted, and the heterojunction becomes *n*<sup>-</sup>–*n*–*p* (or even *p*–*n*–*p*) type. During the subsequent transport of Li ions, the interface potential barrier diminishes and vanishes, and the current–voltage characteristics become ohmic. The importance of doping level control for both the materials is emphasized. The results are applicable for interface engineering in LIB anodes.

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## 1. Introduction

Zinc oxide ZnO is a novel prospective material for lithium-ion secondary battery anodes due to its high theoretical capacity (978 mAh g<sup>-1</sup>), which is three times higher than that of graphite (372 mAh g<sup>-1</sup>). The material is characterized by low cost of the constituent ingredients, good processability, and environmental and health safety in production and recycling. The related oxide semiconductor for LIB anodes is tin oxide. In previous work [1],

graphite was coated with tin oxide by fluidized-bed chemical vapor deposition.

Thin-film electrodes in lithium-ion batteries (LIB) become especially vital in view of battery applications in compact and flexible devices [2]. Interfaces and interphases between different thin layers and grains tend to control the transport of charge carriers (electrons, ions), and reactions leading to an increase in capacity. For example, SnO<sub>2</sub> “nanobaskets” [3] have been fabricated, which exhibited capacity exceeding the theoretical value for bulk SnO<sub>2</sub> (1480 mAh g<sup>-1</sup> instead of 781 mAh g<sup>-1</sup>). This was attributed to the interfacial charging of lithium at the grain boundaries. Improvements are still required to further stabilize the interfacial lithium storage.

The ion transport in poly- and nanocrystalline solids and thin films depends substantially on the space-charge effects at the interfaces [4]. The space-charge regions (SCR) at the interfaces

\* Corresponding author. Tel.: +82 2 958 5252; fax: +82 2 958 5229.

E-mail addresses: [leejk@kist.re.kr](mailto:leejk@kist.re.kr), [joongkee57@naver.com](mailto:joongkee57@naver.com) (J.K. Lee), [alexhodin@msn.com](mailto:alexhodin@msn.com) (A.A. Khodin).

and intergrains could spread and overlap, changing the resulting conductivity type and controlling the ion transport.

Amorphous Si film coated with fullerene C<sub>60</sub> (fullerite layer) has been investigated in previous studies to improve the charging/discharging performance of the anodes [5,6]. In particular, boron doping of the fullerite layer was investigated [7]. The boron atoms in the fullerite lattice improve the first cycling performance of the anode due to enhanced conductivity of the C<sub>60</sub>/Si film system and better transfer of Li ions at the electrode/electrolyte interface (SEI) layer [5].

The scope of the present work is the initial charging process that will set the resulting microstructure and electrochemical features of the anode electrode based on *n*-ZnO/*p*-aSi heterostructure.

## 2. Background

ZnO is presumably an *n*-type wide-bandgap semiconductor, for which the basic dopant is oxygen vacancies. If we consider the first charging processes in an LIB anode, we should analyze the transport phenomena of lithium ions entering the anode structure. Initially, the Li ions will behave as a dopant in the host semiconductor. With Li ions substitution in Zn sites in the lattice, *n*-type doping of ZnO was obtained [8]. Other data demonstrated *p*-type doping of ZnO when Li ions form interstitial defects [9].

The *p*-type conductivity could not be achieved if the total concentration of shallow acceptors does not exceed 10<sup>20</sup> cm<sup>-3</sup> [10]. In a theoretical work [11], the solubility limit was calculated for Li<sub>Zn</sub> acceptors in ZnO as ~10<sup>19</sup> cm<sup>-3</sup>.

Generally, it is important to note the difference between the conductor-type Li-absorbing layers, like carbon, fullerite [12], copper, lithium itself, etc., and semiconductors, like silicon, as a medium band-gap material, or tin oxide, zinc oxide, another wide band-gap semiconductors. In the first case, the Li-absorbing layer always has enough electrons to take part in Li<sup>+</sup> ion coupling. With semiconductors like ZnO, the Li coupling reaction depends on the moving charges (electrons or holes) concentration, or on their external supply. The reaction could be controlled by doping, charge carriers current or photo-injection (in general case) supply. The last mechanism may be involved in prospective experimental cell with transparent packaging to test the effect.

Taking into account the strong exponential-type dependence of the moving charge carriers in a semiconductor on factors such as the doping level, temperature, mechanical stresses (in piezoelectric semiconductors), grain boundary interfacial charge centers, the process of Li ion intercalation/bonding in ZnO should depend much more on external parameters, like ZnO layer processing mode, working conditions, etc.

It is worth comparing the oxygen atoms behavior, as the main base dopant, with another oxide semiconductor SnO<sub>2</sub>. Oxygen vacancies in SnO<sub>2</sub> could diffuse/drift, in both the near-surface (activation energy of ~1.1 eV) and bulk modes (~1.8 eV) [13]. For the first case, near-surface diffusion is possible at room temperature, and for the second, the room-temperature process is almost prevented. In the case of ZnO, the interstitial oxygen is responsible for self-diffusion in *n*-ZnO, and oxygen vacancies are responsible for self-diffusion in *p*-ZnO [14].

The enhanced ion transport along the grain boundaries has been investigated [15]. Lateral diffusion of Li ions along the hetero-junction interface and intergrains boundaries could be more effective than the bulk transport. The small-grain layers would be preferential, so the interface space charge regions become critically important. In this view, the zinc oxide/amorphous silicon hetero-interfaces, as well as inter-grain interfaces, should be analyzed in regard to their electronic features related to charge carriers accumulation and transport processes.

In the case that all the defects (ions) could move and redistribute in the heterostructure's space charge region, the Gouy–Chapman approach is applicable [16]. The one-dimensional flux  $J_{Li}$  of Li ions in the structures under study is controlled by both the diffusion due to the concentration gradient and the drift in the electric field:

$$J_{Li} = -D_{Li} \frac{\partial C_{Li}}{\partial x} + M_{Li} C_{Li} E, \quad (1)$$

where  $D_{Li}$  is the diffusion coefficient,  $C_{Li}$  is the ions concentration, and  $M_{Li}$  is the Li ion mobility in the semiconductor.

At low temperatures, the defects usually have low mobility to move in response to the excess charge at the interface. The depleted defects could be neglected. The charge density is controlled by the dopant concentration, as is the case with the Mott–Schottky approach.

Thus, in conditions where Li<sup>+</sup> ion insertion occurs through the heterointerface during the initial charging, the Mott–Schottky case will dominate when no movable ions are at the interface area. Then, during the lithium ion penetration, the transition to the Gouy–Chapman case should proceed where the movable Li<sup>+</sup> ions and resulting species modify the SCR and compensate for the immobile doping *n*-type centers.

## 3. Results and discussion

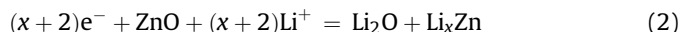
The heterojunctions formed by the *n*-ZnO thin layer on *p*-type amorphous silicon (aSi) were modeled, including varying doping levels of silicon ( $N_A$ ) and zinc oxide ( $N_D$ ) layers, using the corresponding Poisson equation and the charge carrier transport equations. Lithium ion drift/diffusion proceeds much slower than the response of the electron subsystem to the ion movement and corresponding composition changes. Thus, the band structure of the junction could be considered as quasi-stationary for the electron transport at every step.

The general view of the *n*-ZnO/*p*-aSi heterojunction band model is presented in Fig. 1 for varying doping levels of the both layers, aSi and ZnO. The space charge region (SCR) widths vary by up to ~20 nm. Thus, for the typical ZnO grain size of ~50 nm [17], the grains could be depleted almost completely under doping levels less than 10<sup>18</sup> cm<sup>-3</sup>. To obtain maximum efficiency of electric field promotion for Li ions entering ZnO, the thickness should not be more than ~50 nm.

For low-level doped ZnO, the electric field mainly concentrates in this (ZnO) layer (Fig. 2). Lithium ions will undergo this field action under the first charging.

The SCR electric field of the *n*-ZnO/*p*-Si heterojunction forces Li ions to be drawn in from the zinc oxide into the silicon (see Fig. 3). It is more effective to use relatively low-level doped ZnO (less than ~10<sup>18</sup> cm<sup>-3</sup>) for the space charge region extended over the most of this layer's thickness. For the same goal, a relatively low-level doped aSi is required. For these doping levels, the wider SCR' field configuration will be less sensitive to volume changes in Si under Li ions incorporation. And, *vice versa*, the narrow SCR in highly-doped materials will be modified (and destroyed) at the very beginning of Li ions transport at the interface.

At the initial stage of the first charging, the interface electric field controls the charge carriers (electrons and Li ions) in the active zone of the junction. The electrons supply determines the main subsequent electrochemical reaction of Li ions coupling in the layer:



In the heterostructure under investigation, the mobile Li<sup>+</sup> ions

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