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Full Length Article

Preparation of mesoporous carbon nitride structure by the dealloying of Ni/a-CN nanocomposite films

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ABSTRACT

The preparation of mesoporous carbon nitride (p-CN) structure by the selective dealloying process of Ni/a-CN nanocomposite films is investigated. The composition and structure of the Ni/a-CN nanocomposite films and porous carbon nitride (p-CN) films are determined by scan electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and Raman spectroscopy. Phase separated structure including nickel carbide phase and the surrounding amorphous carbon nitride (a-CN) matrix are detected for the as-deposited films. Though the bulk diffusion is introduced in the film during the annealing process, the grain sizes for the post-annealed films are around 10 nm and change little comparing with the ones of the as-deposited films, which is associated with the thermostability of the CN surrounding in the film. The p-CN skeleton with its pore size around 12.5 nm is formed by etching the post-annealed films, indicative of the stability of the phase separated structure during the annealing process.

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1. Introduction

Mesoporous carbon structure with the high specific surface area has attracted significant attention during the past few decades because of their excellent properties on the applications of filtration [1], hydrogen storage devices [2,3] and the electrocatalyst of the ORR (oxygen reduction reaction), which is fundamental in various energy storage and conversion devices [4,5], etc. The doping of N atoms in the porous carbon structure can change the surface and porous structure and improve its hydrophilic property and electron transport rate, which can widely expand its application [6,7]. The conventional mesoporous carbon or carbon nitride structure is synthesized by the pyrolysis and physical or chemical activation of organic precursors [1–7], from which porous carbon (p-C) or carbon nitride (p-CN) structures with tunable pore size and structure can be obtained. Except for the typical methods, Bouts et al. [8] applied the dealloying concept [9–11] on Cu/C nanocomposite films and the porous carbon films with a tunable pore size of 2–11 nm were obtained. During the dealloying process, the metal or the sensitive phase is etched and the remained porous structure can be the presentation of the surrounding skeleton. The selective etching method has been successfully used for the totally non miscible element based films, which has the very different oxidation potentials between the two phase included, such as Al/Si and Al/Ge films [12,13], Ag/Au films [14], Pt/Cu and Pt/Si films [15,16]. The pore size and structure can be used to clearly reflect the effect of deposition parameters on the films as well as the deposition and structure evolution mechanism to some extent. However, the requirement of the totally non miscible nature of the involved elements during the dealloying process restricts its further application on the nanocomposite films.

Nickel is of interest for the researchers in many applications, not only because of the excellent electromagnetic and chemical properties of phase separated Ni/C nanocomposite films [17–19], but also its important catalytic effect on the growth of carbon-based nanostructures, which has widely used for the preparation of CNT, carbon nanowires, graphene and nanogriphite materials [20–24]. Considering the low affinity with carbon, nickel typically exists as carbide during the preparation of nickel carbon nanocomposite films under room temperature [17–20]. The noble nature of nickel carbide towards acid solution restricts the application of the dealloying process on the Ni/C nanocomposite film for the preparation of mesopore structure [25]. According to the C-Ni (carbon-nickel) system summarized by Singleton and Nash [26], the carbon content of Ni_3C is around 25 at.% while fcc Ni has a maximum carbon solubility of only 0.01 at.%, thus the metastable Ni_3C phase tends to isothermally decompose into the metallic fcc Ni phase under the temperature higher than 300 °C. Bayer et al. focused on the phase transition of the Ni/C nanocomposite films during

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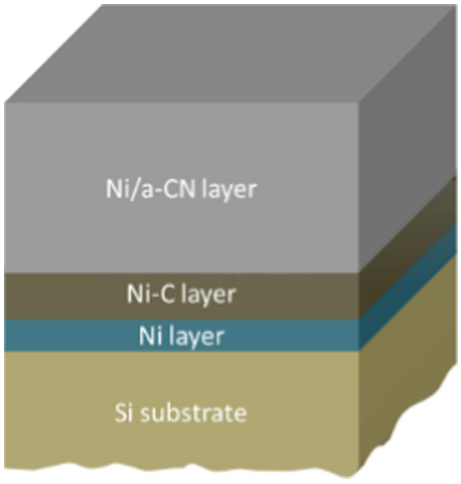

Fig. 1. Schematic diagram of the Ni-C nanocomposite film deposition sequence.

the annealing process, and the phase transition accompanying with the film structure evolution from homogenous to vertically separated structure was observed [27]. Schaefer et al. prepared the hollow carbon balls by applying the transition of the Ni_3C to fcc Ni phase and the following etching process, from which the fcc Ni core obtained by annealing the initial Ni_3C phase in the carbon shell was dissolved [28]. Though the p-CN film is widely prepared by the chemical activation [5–7], the formation of the p-CN film by applying the dealloying process on the Ni/CN nanocomposite film is rarely investigated.

Herein, we propose a method for the preparation of p-CN structure by etching the post-annealed Ni/a-CN nanocomposite films in HCl solution. Filtered cathodic vacuum arc deposition (FCVAD), which is outstanding among the deposition techniques because of the high ionization rate and the effect of ion bombardment during the deposition, was used for the Ni/a-CN nanocomposite film preparation. The annealing process on the structure and phase evolution and the mechanism of the formation of the p-CN structure are also investigated.

2. Experiment details

2.1. The preparation of Ni/a-CN nanocomposite films

The Ni/a-CN nanocomposite films were deposited on (1 0 0) single crystalline silicon wafers and (1 0 0) NaCl crystal by filtered cathodic vacuum arc system in a mixed C_2H_2 and N_2 atmosphere. The schematic of the device is given elsewhere [29]. Briefly, a 100 mm in diameter and a purity of 99.99% of Ni cathode was triggered to produce Ni plasma at a constant arc current of 100 A. The Ni plasma was then effected by an electromagnetic field and imported into the vacuum chamber through a 90° bent duct and collided with C_2H_2 and N_2 gas to form the mixed plasma. The base pressure of deposition chamber was adjusted to $3 * 10^{-3}$ Pa before the experiment and the substrate bias was −200 V. Pure nickel transition layer followed by a Ni-C transition layer deposited under a gradient voltage (−200 V to 1000 V) and C_2H_2 flow rate were used to increase the adhesion between Ni/a-CN film and Si substrate and impede the diffusion of the silicon atoms into the films during the annealing process. During the experiment, the carbon content changed from 56 sccm to 180 sccm while the N_2 flow rate keeps constant at 42 sccm in all situations. By changing the incoming of the C_2H_2 flow rate, the films with the carbon content of 24.6 at.%, 45.1 at.%, 53.7 at.% and 63.3 at.% were selected for the investigation, while the N content keeps around 5.0–8.6 at.% in these films. The schematic diagram of the deposited films is shown in Fig. 1.

2.2. The preparation of the p-CN films

The Ni/a-CN nanocomposite films were first annealed at the temperature of 600 °C in a vacuum furnace with a base pressure of 0.5 Pa. The heating rate kept at 13.5 °C/min for all the samples

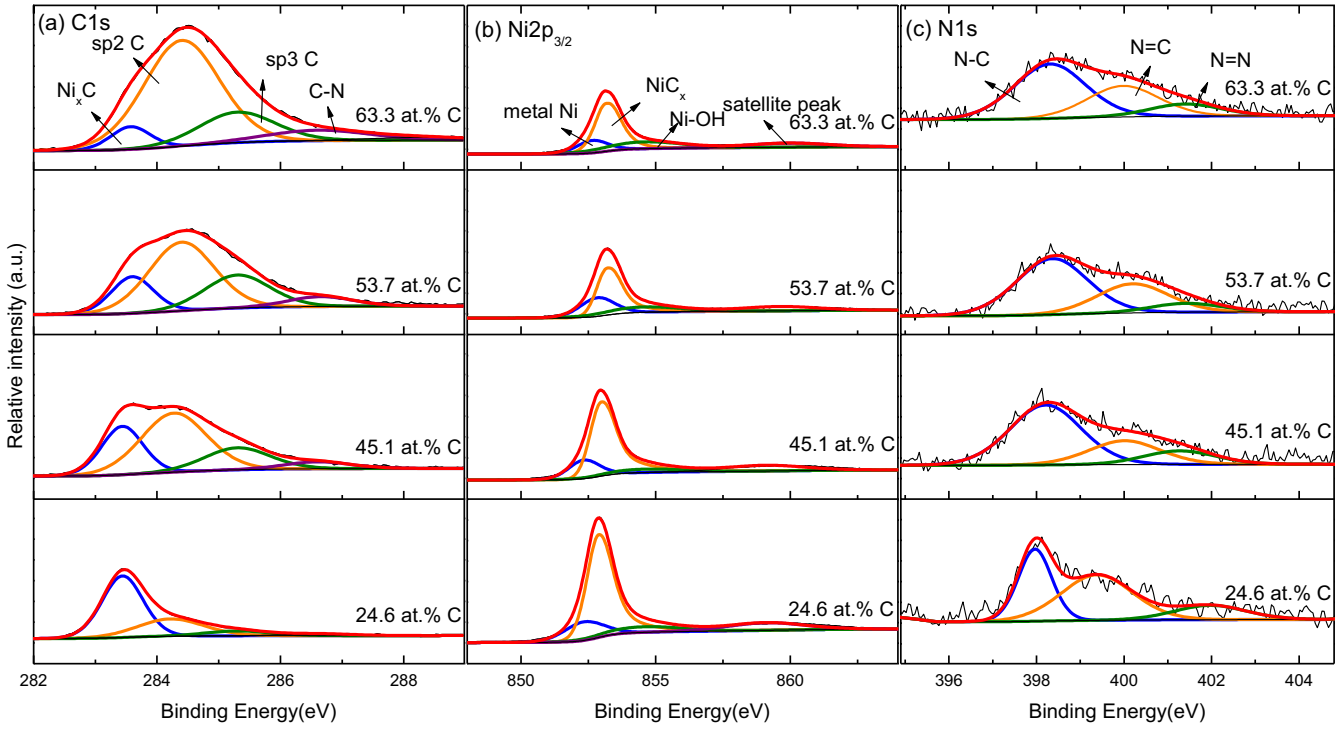

Fig. 2. (a–c) The XPS spectra of C1s (a), Ni2p3/2 (b) and N1s (c) for the as-deposited Ni/a-CN films under different carbon content.

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