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Electroless deposition of nickel-phosphorous nano-dots for low-temperature crystallization of amorphous silicon

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ABSTRACT

Metal-induced crystallization (MIC) of amorphous silicon (a-Si) is an effective approach for low-temperature formation of polycrystalline silicon thin films. In this study, Ni-P nano-dots were directly deposited on amorphous silicon using a non-isothermal deposition (NITD) method without complicated pretreatment such as surface activation and sensitization. The density of these dots can be controlled by governing the process parameters such as reacting time and substrate temperature. Crystallization of Si was then achieved by annealing at 550 °C. It was found that Si crystallinity increased with Ni deposition time and temperature, and the amorphous Si film was fully crystallized after annealing when Ni-P was deposited at 200 °C for 30 s. We believe this technique can expand the applicability of electroless plating (EP) to metal-induced low-temperature growth of polycrystalline Si films.

1. Introduction

There is an ever-increasing demand for fabricating polycrystalline silicon (poly-Si) films on glass or plastic substrates due to their applications in thin-film transistors (TFT) and solar cells. Solid phase crystallization is a widely-used method for forming poly-Si out of amorphous silicon (a-Si) films, but its high annealing temperature at 600 °C precludes the use of normal glass substrates. Intensive studies have been performed to lower the crystallization temperature of a-Si films grown on glass substrates. Among them, metal-induced crystallization (MIC) or metal-induced lateral crystallization (MILC) offers many advantages such as low cost, simplicity, large-area capability, and high carrier mobility [1,2]. In MIC or MILC, a thin layer of metal catalysts (Ni [1–5], Pd [6], or Al [7]) was deposited on an a-Si film, usually by physical vapor deposition (PVD), or more recently, electroless plating (EP) [2,8], followed by crystallization at a temperature lower than 600 °C.

The EP Ni method was introduced by Y.C. Chen et al. [8] to replace PVD in MIC or MILC. It is much cheaper, simpler and faster than PVD. In addition, they found that the morphologies and device characteristics of the MILC poly-Si TFT fabricated by EP Ni were as good as those by PVD Ni [2]. However, for non-metallic substrates, conventional EP generally requires complicated surface pretreatment such as chemical etch, sensitization, and activation. Usually activators containing precious metal Pd are needed in this process. In this work, we employed a non-isothermal deposition (NITD) method [9–12] derived from conventional EP to deposit Ni nano-dots on a-Si films for MIC. Owing to its unique design, a high-temperature deposition zone in the NITD reactor allows electroless deposition of metal films on non-metallic substrates such as glasses, ceramics, indium tin oxide, silicon wafers, polymeric materials, etc., without sensitization and activation.

In our former studies [13,14], NITD has proven useful in the deposition of catalyst dot arrays for carbon nanotube growth. Here we demonstrate its application in the formation of metal-induced low-temperature poly-Si (LTPS). This technique has many advantages other than eliminating the use of noble metals and simplifying the processes. For example, it offers higher deposition rates while maintaining good stability against self-decomposition of the plating bath; it is more flexible in that more key parameters such as the substrate temperature, the reacting time, the clearance width between substrate and heater, the amount of stabilizer, etc. can be operated independently. Most importantly for this application, it shows an ability to deposit metal dots with nanometer size, which is good for minimizing metal contamination in silicon after annealing. It is very important, for example, in thin-film c-Si solar cells to control the Ni concentration in order to avoid major carrier-recombination problem [15].

2. Experiment

The details of our NITD method have been described in our previous articles [9–12]. In our design, the deposition temperature of the substrate (T_s) and the bath (T_b) can be operated independently. The

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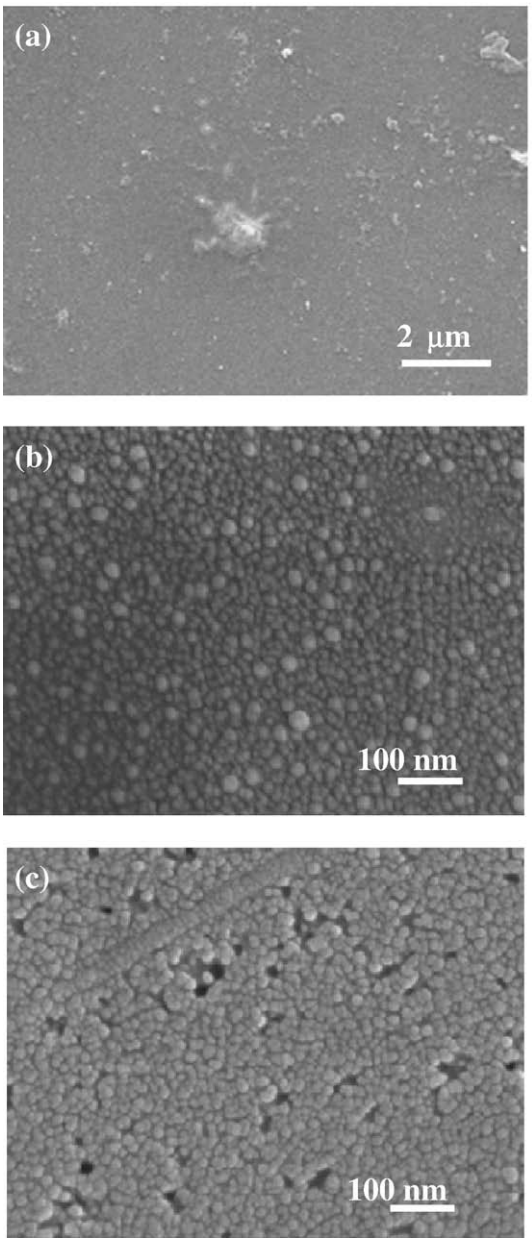

Fig. 1. SEM morphologies of Ni-P catalysts deposited by NITD technique at T_s=(a) 100, (b) 160, and (c) 200 °C. The deposition time is 30 s.

high T_s enhances the reduction of metal ions into metallic nanoparticles and forces the metallic primary nuclei to deposit on the substrate. Meanwhile, the low T_b restrains the undesired decomposition reaction in the bath and thus lengthens the bath life. The difference between T_s and T_b can be hundreds of Kelvin.

The substrates used in this experiment are a-Si coated glass plates. The thickness of a-Si is 200 nm. The samples were first degreased in a mixed solution of H_2SO_4 and H_2O_2 using ultrasonic treatment for 30 min, and then washed with deionized water. These cleaned samples were then etched for 15 s in 5% HF solution to remove the native oxide. Ni-P nano-dots were deposited onto the substrates using NITD technique with the plating solution composed of $NiSO_4 \cdot 6H_2O$ 30 g/L, $NaH_2PO_2 \cdot H_2O$ 30 g/L, $C_3H_5O_3Na$ 40 g/L, $C_2H_5O_2$ N 10 g/L, and surfactant (DisperAnion H14 N, Sino-Japan Chemical) 20,000 ppm, and adjusted to pH 9 by adding ammonium hydroxide. We also tried to deposit pure Ni dots by replacing the reducing agent NaH_2PO_2 with N_2H_4. It has been reported that the presence of phosphorous can promote the formation of disilicide $NiSi_2$ at low temperature [16], which helps the crystallization of a-Si because the disilicide precipitates act as nucleation sites and crystallization proceeds via the migration of precipitates through a-Si [17]. For example, Hayzelden et al. [17] reported that $NiSi_2$ precipitates were observed *in situ* to migrate though the a-Si leaving a trail of crystalline Si formed on {111} faces of the octahedral $NiSi_2$ precipitates with a coherent interface, and the growth rate of the crystalline Si was limited by diffusion through the $NiSi_2$ precipitates. Liu et al. further observed that the presence of P in the electroless Ni films resulted in a thin layer of Ni_3P between Ni and Si [16]. This stable Ni_3P phase reduced the supply of Ni atoms through the electroless Ni/Si interface and thus promoted the formation of disilicide $NiSi_2$, instead of monosilicide (NiSi), at low temperature. In our study, we found that, indeed, the crystallinity and grain size of the LTPS induced by Ni-P were better than those by pure Ni.

The bath temperature was set at 20 °C, and various values of T_s between 100 and 200 °C were used. The deposition time was varied

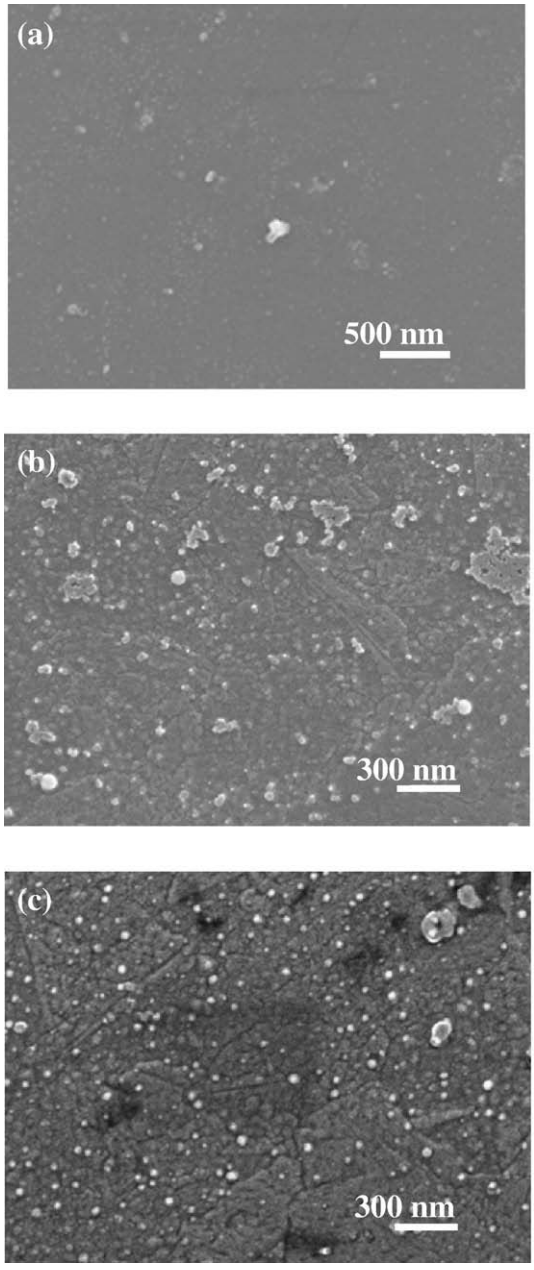

Fig. 2. SEM images of the samples after annealing at 550 °C for 20 h. The Ni-P catalysts were deposited at (a) 100, (b) 160, and (c) 200 °C, for 30 s.