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To cite this article: Chunyu Guo, Yini Fang, Bin Wu, Si Lan, Guo Peng, Xun-li Wang, Horst Hahn, Herbert Gleiter & Tao Feng (2017) Ni-P nanoglass prepared by multi-phase pulsed electrodeposition, Materials Research Letters, 5:5, 293-299, DOI: [10.1080/21663831.2016.1264495](https://doi.org/10.1080/21663831.2016.1264495)

To link to this article: <https://doi.org/10.1080/21663831.2016.1264495>



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Published online: 12 Dec 2016.



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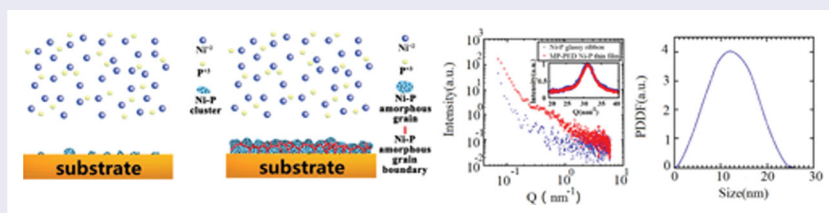
Ni-P nanoglass prepared by multi-phase pulsed electrodeposition

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ABSTRACT

Ni-P nanoglass consisting of nanometer-sized amorphous grains separated by amorphous interfaces was prepared by a specially designed multi-phase pulsed electrodeposition technique. The microstructure of the deposited Ni-P nanoglass was confirmed by X-ray diffraction, high-resolution transmission electron microscopy, small-angle X-ray scattering, and X-ray photoelectron spectroscopy. The formation of the Ni-P nanoglass, which is characterized by inhomogeneities on the nanometer length scale, is achieved via proper control of the rate of cluster formation and cluster growth by a multi-phase pulsed electrodeposition process.



ARTICLE HISTORY

Received 30 September 2016

KEYWORDS

Nanoglass;
electrodeposition;
microstructure; interface

This paper deploys a specially designed multi-phase pulsed electrodeposition method to fabricate the Ni-P nanoglass, and opens a window for developing amorphous alloys with tunable atomic-to-nanoscale heterogeneous microstructure.

The development of new materials and the optimization of properties of materials used in today's technology are based on the controlled modification of their microstructure, which has so far been limited to crystalline materials. A similar approach has not been possible so far for amorphous materials, mainly because today's amorphous materials are produced almost exclusively by rapid quenching from the melt. Hence, it is not surprising that the atomic structure of the amorphous materials resembles that of the molten state frozen at the glass transition temperature. Obviously, the production route via the molten state does not permit the introduction of micro-structural features into glasses. The discovery of nanoglasses has opened a possible new route towards bulk amorphous structures [1–4], which results

in structural inhomogeneities on the length scale of a few nanometers.

Nanoglasses are a new kind of non-crystalline materials [1–4] consisting of amorphous nanometer-sized grains connected by amorphous interfaces (called glass/glass interfaces). It has been found that the interfaces have an atomic and electronic structure deviating from those of the adjacent amorphous grains. As a result of the different atomic and electronic structures of the glass/glass interfaces, the properties of nanoglasses differ from the properties of the melt-quenched glass with the same chemical composition. As an example, it has been found that a Fe₉₀Sc₁₀ nanoglass is ferromagnetic at 300 K, whereas the corresponding melt-quenched glass is paramagnetic, and only exhibits ferromagnetic order at a temperature below 200 K [5]. Moreover, nanoglasses have been reported to be more ductile, more biocompatible, and catalytically more active compared to the corresponding melt-quenched glasses [6–14]. Hence, by modifying the microstructure of nanoglasses using

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Supplemental data for this article can be accessed here. <http://dx.doi.org/10.1080/21663831.2016.1264495>

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controlling the size of the amorphous grains (i.e. the volume fraction of the interfacial regions) and/or by varying their chemical compositions [2–4], the properties of nanoglasses may be modified in a controlled manner.

The original and most frequently used route to nanoglasses has been the consolidation of nanometer-sized amorphous clusters previously generated using inert gas condensation (IGC) [5,10] or by magnetron sputtering (MS) [8,9]. Moreover, severe plastic deformation (SPD) has been applied recently to produce glasses with nanometer-sized microstructure [15,16].

The understanding of nanoglasses that focuses on the understanding of both the atomic and the electronic structure of the glass/glass interfaces is the key consideration. However, studies of the glass/glass interfaces require the availability of nanoglasses with uncontaminated interfaces. Despite the fact that IGC is performed under well-controlled experimental ultra-high vacuum conditions, contamination of the glass/glass interfaces in nanoglasses prepared via this route cannot be excluded [5,10]. Studies of nanoglasses prepared by MS revealed a nano-columnar growth and interfacial segregation [17]. SPD seems to be a promising technique for the production of nanoglasses with a large fraction of shear bands. However, it remains to be proven that the structures of the glass/glass interfaces in SPD structures are comparable to that of nanoglasses prepared by IGC or MS [15,16]. In any case, the development of new preparation methods for nanoglasses seems desirable to explore the full potential of the new materials.

Here, we report on a new method for preparing nanoglasses based on electrodeposition. Pulsed electrodeposition has been reported to result in high-purity nano-crystalline materials with the large volume fraction of crystal/crystal interfaces, i.e. grain boundaries [18–21]. Furthermore, electrodeposition is a widely adopted method to prepare amorphous films [22–25]. Hence, a multi-phase pulsed electrodeposition (MP-PED) was developed to prepare high-purity amorphous films with structural features on the nanometer scale. The microstructure of MP-PED prepared Ni-P nanoglass was studied by X-ray diffraction (XRD), high-resolution transmission electron microscopy, small-angle X-ray scattering (SAXS), and X-ray photoelectron spectroscopy (XPS). The results obtained from these studies demonstrate that the MP-PED technique is an economical and effective way to produce high-purity nanoglasses.

The Ni-P nanoglasses were prepared as follows: a conventional three-electrode cell and an electrochemical workstation were used for the electrodeposition process. Pre-cleaned copper substrates were used as working electrodes. The counter electrode and the reference electrode were a platinum sheet and a saturated calomel

electrode, respectively. Analytical grade reagents (Merck) were used for the electrodeposition of the Ni-P nanoglass. Before the deposition process, the substrate was polished mechanically with silicon carbide emery paper and chemically treated in 10% sulfuric acid for 1 min. After these pre-treatment steps, the substrates were cleaned in acetone and then rinsed thoroughly in double distilled water. The distance between the anode and the cathode was maintained at 10 mm to ensure uniform deposition. During deposition the electrolyte was stirred with a magnetic stirrer. The bath compositions and deposition conditions are summarized in Table 1. Boric acid (H_3BO_3) was added as supporting electrolytes and as pH buffer. The applied voltage was varied during the electrodeposition process in the form of three steps. During the first step, a high voltage of 9 V was applied for $t_{\text{on1}} = 1$ ms. The second step consisted of the application of a lower voltage (5 V) for $t_{\text{on2}} = 19$ ms. During the third and last step, the voltage was turned off for $t_{\text{off}} = 20$ ms. This procedure was applied for a deposition time of 1–3 h. The relationship of applied voltage and time was presented in the supplement figure. The thickness of the film was measured using a cross-section profile with field emission scanning electron microscopy. In fact, the thickness of the film was found to increase proportionally to the deposition time, from which the deposition rates were estimated to be 5.33 ± 0.12 nm/s. The chemical composition of the Ni-P films for further characterizations was measured to be $\text{Ni}_{78}\text{P}_{22}$ (± 2 at%, with conditions of $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ 180 g/L and H_3PO_3 15 g/L) using energy-dispersive X-ray spectroscopy analysis.

XRD (Bruker D8 with Mo source) and transmission electron microscopy (FEI Titan 80-300) studies were utilized to show the amorphous structure of the MP-PED Ni-P films. A few broad peaks, typical for amorphous structures, are revealed (Figure 1(a)) in the X-ray diffraction pattern. Figure 1(b) shows a high-resolution transmission electron micrograph of an MP-PED film after thinning by focused ion beam (ZEISS AURIGA). The maze-like pattern in the micrograph (visible in Figure 1(b)) is a characteristic feature well known

Table 1. Electrolyte composition and deposition conditions.

Electrodeposition conditions	Values
Electrolyte	
$\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$	180–220 g/L
$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$	25 g/L
H_3PO_3	15–25 g/L
H_3BO_3	28 g/L
Operating conditions	
Temperature	50°C
pH	1
Total electrodeposition time	1–3 h

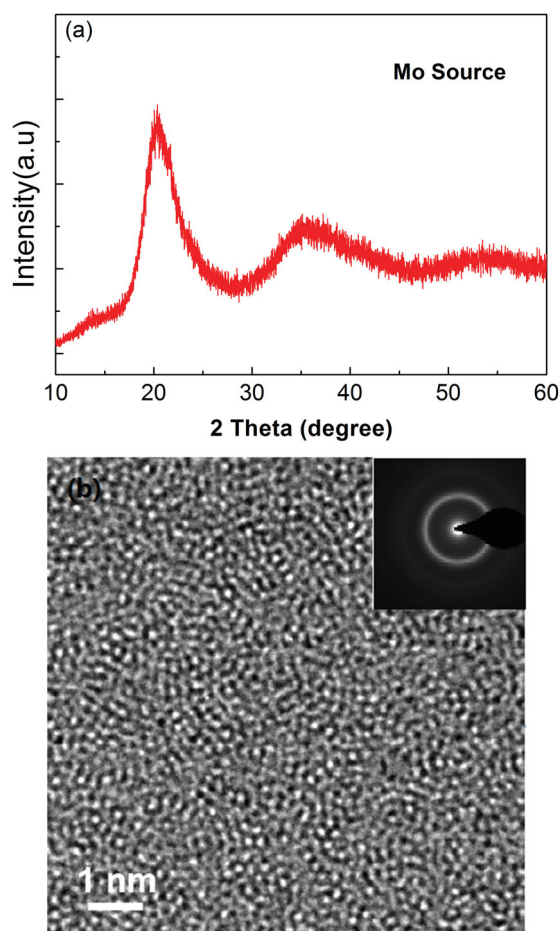


Figure 1. (a) XRD pattern of a MP-PED Ni-P film and (b) high-resolution transmission electron micrograph of a MP-PED Ni-P film. The inset in (b) is the SAED pattern of the MP-PED Ni-P films.

for amorphous materials. The selected area electron diffraction (SAED) pattern (inset in Figure 1(b)) with halo rings further confirms the amorphous structure of the MP-PED Ni-P films. No spots on the halo rings were observed which would indicate signs of partial crystallization.

Figure 2 shows a scanning electron micrograph of the surface morphology of a MP-PED Ni-P film without any treatment. It reveals granular structures with a brighter contrast joined by interconnected darker regions. The latter regions can be associated with the glass/glass interfaces, as previously done in other nanoglass structures [1–4]. In nanoglasses prepared by IGC, small-angle X-ray scattering studies [10] indicated that these interfacial regions have a lower density than the adjacent amorphous grains. As the preparation of nanoglasses using consolidation of amorphous nanoparticles (synthesized by IGC) is completely different from the electrodeposited dense amorphous film, it is an open question whether the two different synthesis routes lead to identical or different amorphous structures. The presence of the contrast

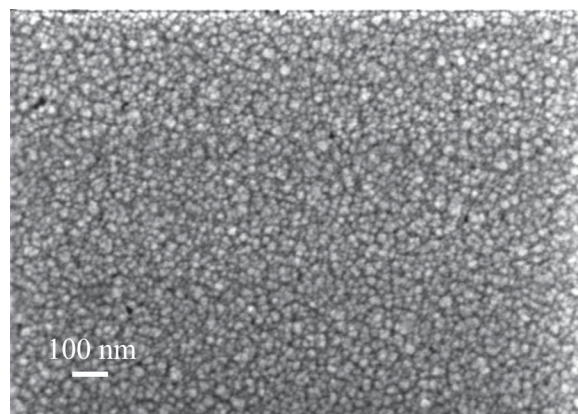


Figure 2. SEM image of the surface morphology of a MP-PED Ni-P film without any treatment. It reveals granular structures with brighter contrast joined by interconnected darker regions. The latter regions can be associated with the glass/glass interfaces.

between grains and interfacial regions between the grains as clearly seen in Figure 2 is a strong indication that the amorphous nature of the electrodeposited amorphous Ni-P is rather different from that of melt-spun amorphous ribbons of the identical material. In any case, it is obvious that the MP-PED process leads to an amorphous structure in the Ni-P system with inhomogeneities on the scale of nanometers. In order to obtain further information on the nature of these inhomogeneities, SAXS and wide-angle X-ray scattering (WAXS) measurements have been performed. Figure 3(a) shows the SAXS and WAXS results for the MP-PED Ni-P thin films and, for comparison, the Ni-P amorphous melt-spun ribbon with the identical chemical compositions. The measurements were performed using an Anton Parr SAXS pace instrument with Mo target. All samples had a thickness of $\sim 30 \mu\text{m}$. The WAXS data (inset in Figure 3(a)) display nearly an identical feature for the first (diffuse) diffraction peak for both samples. This result indicates that the short range atomic order is similar to both materials. However, in comparison to the SAXS profile for Ni-P amorphous ribbons, the SAXS scattering intensity for the MP-PED Ni-P thin films increases more rapidly below 2 nm^{-1} . SAXS profile of MP-PED Ni-P thin film displays a pronounced hump at $\sim 0.5 \text{ nm}^{-1}$ as compared to that of amorphous ribbon, which is similar to the result of Fe-Sc nanoglass prepared by IGC [10]. Furthermore, this result implies that the MP-PED Ni-P thin films have a granular structure with a pair distance distribution function (PDDF) of the grains as shown in Figure 3(b). We obtained PDDF by using GIFT software integrated with the indirect Fourier transform (IFT) technique [26]. The Q range used for IFT is $0.18\text{--}5 \text{ nm}^{-1}$. It reveals the possible grain size in the MP-PED Ni-P thin films. The maximum diameter is $\sim 26 \text{ nm}$. This analysis is clear evidence

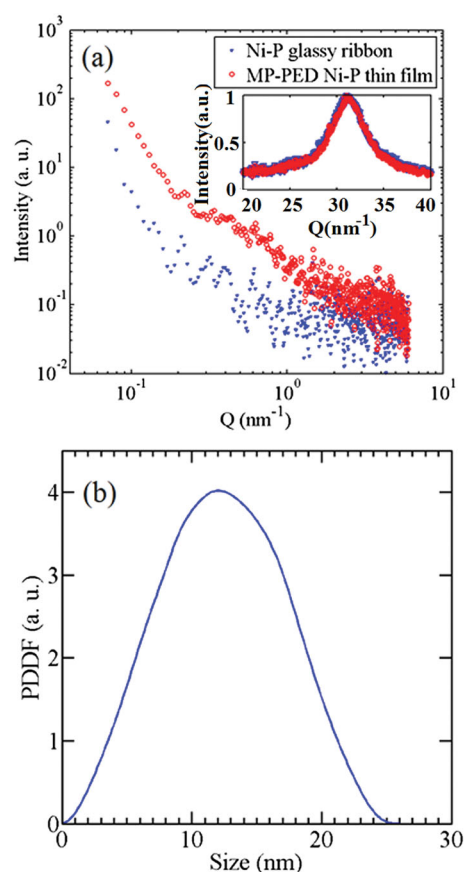


Figure 3. (a) SAXS results for MP-PED Ni-P thin films (red) and Ni-P amorphous melt-spun ribbons with identical chemical compositions (blue). The SAXS profile of the MP-PED Ni-P thin films displays a pronounced hump at $\sim 0.5 \text{ nm}^{-1}$ as compared to that of the amorphous ribbon, which is consistent with the feature of IGC nanoglass [10]. The inset in (a) is the WAXS data of MP-PED Ni-P thin films (red) and Ni-P amorphous melt-spun ribbons, respectively; (b) the size distribution, PDDF, deduced from the SAXS data for the MP-PED Ni-P thin film by IFT.

of the inhomogeneous structure of the MP-PED Ni-P films, which is compatible with the model of nanoglasses as described in the literature [1–4,10].

The depth profile of the elemental composition of the MP-PED Ni-P films was measured by XPS and Ar^+ ion sputtering in the PHI 5000 Versa Probe II system. All XPS measurements on the MP-PED Ni-P films were obtained using monochromatic $\text{Al K}\alpha$ X-ray radiation ($h\nu = 1486.6 \text{ eV}$). The calibration was performed by matching the C 1s peak from carbon contamination on the sample surface to 284.8 eV. The depth profile of the elemental composition of the films was studied by removing thin layers by Ar^+ ion sputtering. The sputtering procedure was applied in steps of 1 min duration. The ion energy was 4 kV. The size of the sputtered area was $2 \text{ mm} \times 2 \text{ mm}$, and the number of cycles for every XPS measurement was 5. The XPS analysis was carried out

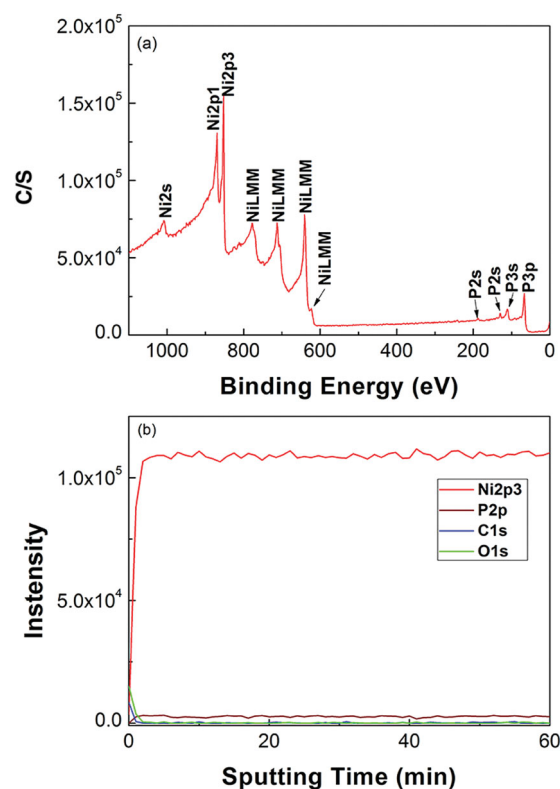


Figure 4. (a) An overview XPS spectrum of a MP-PED Ni-P film after a total time of Ar^+ ion sputtering of 10 min and (b) the depth profile of the MP-PED Ni-P films with Ar^+ ion sputtering for 60 min.

after every sputtering step. Figure 4(a) shows an overview XPS spectrum of a MP-PED Ni-P sample after a total time of Ar^+ ion sputtering of 10 min. All peaks visible originate from Ni and P without any indications of contaminants. Figure 4(b) displays the depth profile of a MP-PED Ni-P film. Clearly, at the surface of the films, contamination with carbon and oxygen is revealed. However, after 1–2 Ar^+ ion sputtering cycles, no more C and O contamination was detected. The high purity of the MP-PED Ni-P films is extremely important further to investigate the atomic and electronic structure of glass/glass interface and understand the structure–property relationship of nanoglasses [3,5,10].

Ni-P amorphous alloys obtained by electrodeposition have been studied in the past for several decades and they have been utilized in various industrial devices due to their attractive magnetic and mechanical properties as well as their good corrosion and wear resistance [27–31]. However, the methods for controlling the micro- and nanostructure of the electrodeposited amorphous Ni-P alloys have not been studied in detail.

To discuss the processes involved in the production of the MP-PED Ni-P films reported in this paper, the electrodeposition growth mechanism of pure Ni will be considered first. The growth mechanism of Ni during

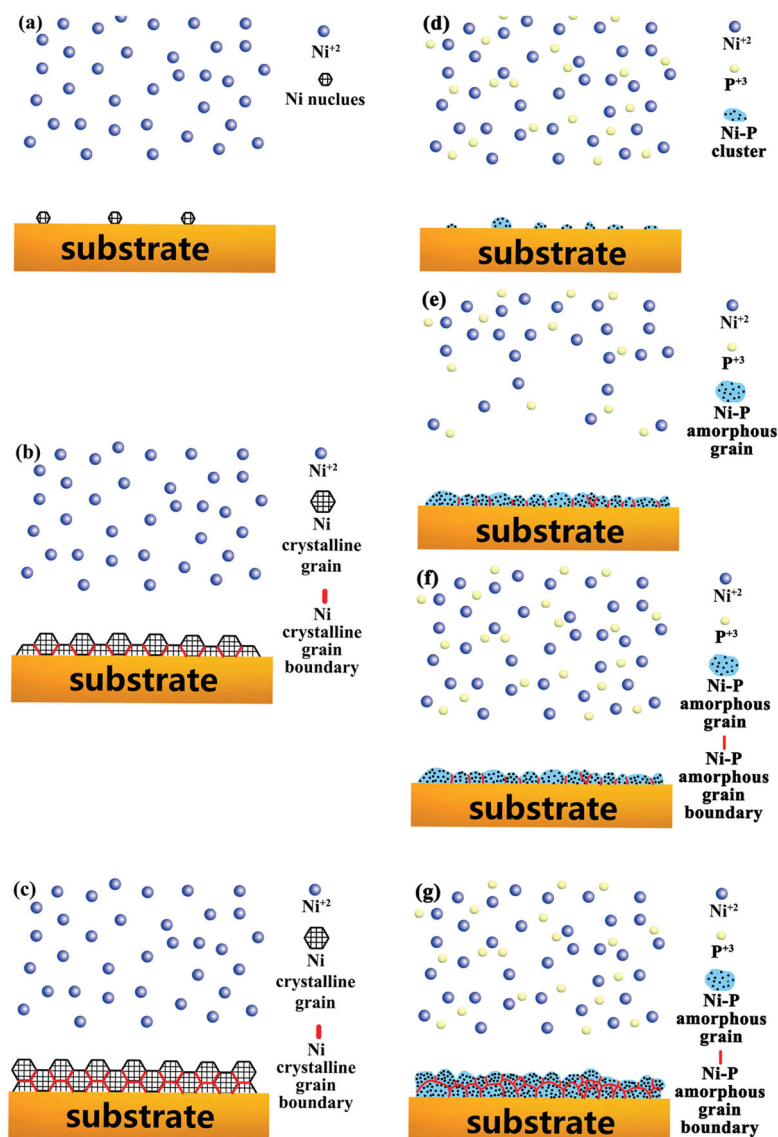


Figure 5. (a)–(c) Schematic of the mechanism of the Ni crystal electrodeposition growth and (d)–(g) schematic of the mechanism of the nanoglass MP-PED Ni-P film electrodeposition growth.

electrodeposition is well known to involve two steps as indicated in Figure 5(a)–(c). In the first step (Figure 5(a)), Ni ions are reduced and deposited leading to the formation of Ni nuclei. The second step (Figure 5(b)) involves the growth of these nuclei resulting in nanometer- or micrometer-sized Ni crystals [21,32–35]. The final size of the Ni crystallites can be controlled by the over-potential of the cathode. By applying a high over-voltage/high current density in pulsed electrodeposition, pure Ni films with nanometer-sized crystallites connected by grain boundaries have been obtained [21,32–37].

A similar mechanism seems to occur during the growth of amorphous MP-PED Ni-P films reported in this paper. During electrodeposition of Ni-P, it is well known that the amorphous structure is determined by the P content of the deposited films [22,31]. If the P

content is kept in the range of 15–25 at%, the growth mechanism of the resulting amorphous Ni-P films is likely to involve the three processes displayed in Figure 5(d)–(g): (1) reduction and co-deposition of Ni and P ions, (2) formation of Ni-P clusters, and finally (3) growth of Ni-P clusters.

If the applied voltage/current density is increased, the size of Ni-P amorphous grains is reduced (similar to the reduced size of electrodeposited Ni crystals). However, increasing the voltage/current density will increase the deposition rate of Ni and reduce the deposition rate of P [22,24] so that instead of forming an amorphous structure, crystallization of the electrodeposited Ni-P films will occur.

The key idea of the multi-phase pulsed electrodeposition technique developed here is that the appropriate

control of the rates of formation and growth of clusters, thus opening the way to produce nanostructured amorphous Ni-P films with a variety of different structures. In fact, by selecting multi-phase pulses with different duration and voltage levels, the formation and the growth processes of the clusters could be controlled as indicated in Figure 5(d)–(g). At the first stage (Figure 5(d)), the Ni-P cluster formation process occurs under the high applied voltage. The high cathode over-potential will result in smaller critical cluster sizes so that the cluster forming energy will decrease, and the cluster formation rate will increase. However, high applied voltages will also reduce the deposition of the phosphor. This variation of the chemical composition will finally cause the amorphous Ni-P clusters to contain some Ni crystals or Ni-P crystals. At the second stage (Figure 5(e)), the applied voltage is reduced and hence the P deposition rate is increased so that an amorphous Ni-P structure is formed. This stage is the Ni-P cluster growth period. The parameters of the growth period can be selected to keep the amorphous grains in the nanometer size regime. At the third stage (Figure 5(f)), the applied voltage is shut down to rebalance the deposition process so that a uniform chemical composition of the Ni-P clusters results. The repetition of these three deposition cycles results in the formation of a Ni-P nanoglass with nanometer-sized amorphous grains and amorphous grain/grain interface (Figure 5(g)).

Compared to the IGC and the sputtering techniques, the multi-phase pulsed electrodeposition technique is a low-cost technique to produce high-purity nanoglasses in the form of thin films. It seems suitable also for industrial applications as it does not require any expensive vacuum technologies and has the potential to be scaled up to produce large area coatings and free-standing films.

Disclosure Statement

No potential conflict of interest was reported by the authors.

Funding

This work was supported by the National Natural Science Foundation of China (grant number 51571119, 51501090, 51520105001), the Natural Science Foundation of Jiangsu Province (grant number BK 2014021775) and the Fundamental Research Funds for the Central Universities. XLW acknowledges the support by the Research Grants Council of Hong Kong Special Administrative Region (CityU Project No. CityU 122713).

Acknowledgements

TF acknowledges the support by the innovation project and the specially appointed professor project of Jiangsu province.

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