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Preferred Orientation Control of Bi Deposits Using Experimental Strategies

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Based on the experimental strategy of fractional factorial design (FFD) and path of the steepest descent/ascent (PSD/PSA), the preferred orientation ratio of Bi(110)/Bi(012) facets of Bi deposits electroplated under a direct-current (dc) mode could be precisely controlled and predicted. The intensity ratio of Bi(110)/Bi(012) facets (i.e., the preferred orientation ratio which is denoted as *f*) was employed as the response variable since this variable was found to be one of the key factors determining the sensitive ability of bismuth-film electrodes (BFEs) to Sn(II). In the FFD study, temperature of the plating bath was identified to be the key factor affecting the preferred orientation ratio of Bi deposits meanwhile *f* only weakly depended on pH, current density, and stirring rate. From the PSD/PSA study, a simple but reliable model for changing the preferred orientation ratio was constructed and the deposit plated at 28°C and pH = 4.25 showed the highest *f* value. Moreover, BFEs with various *f* values could be easily prepared and controlled, meanwhile the morphologies of Bi deposits with different *f* values were also examined in this work.

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Bismuth-film electrodes (BFEs) have been used as an alternative to replace mercury-film electrodes (MFEs) for the determination of heavy metal ions since 2000s.[1] The most significant advantage of BFEs is the environmentally friendly property since the toxicity of bismuth and its salts is negligible.[2] However, the unique analytical ability of BFEs in detecting heavy metal ions, roughly comparable to that of MFEs, has been attributed to the formation of ''fused alloys'' with heavy metals for bismuth. This property, analogous to the amalgams that mercury forms,[3] usually leads to use a stripping solution containing Bi(III)[4] or Bi oxide nanoparticles on substrates[5] for sensing heavy metal ions. The former method is generally complicated because of introducing the detecting solutions into the stripping solution. The second method usually involves the dispersion issue of Bi oxide nanoparticles onto the substrate for promoting the sensing ability. Accordingly, understanding the relationship between the microstructures and the heavy metal ions sensing ability of metallic Bi films is important for the future applications of BFEs.

There are several methods, such as thermal evaporation,[6] electrodeposition,[6–9] DC sputtering,[10] RF magnetron sputtering,[11] and molecular beam epitaxy,[12] etc., for preparing BFEs. From a comparison of these methods, electrodeposition is a simple route which shows the ability for controlling the morphology, roughness, grain sizes, and preferred orientations of metals and alloys via changing the electroplating solutions such as composition,[13,14] pH,[15] complex agents,[16] and additives[17,18] as well as the deposition parameters e.g., current density[13] and deposition mode,[19–21] etc. However, to date, electrodeposition of bismuth films with good qualities (e.g., uniformity, good adhesion, etc.) is still recognized as a challenge.[22] Moreover, little literature has been published to establish the relationship between the microstructure and the metal ion sensing ability of BFEs[23] and to control the morphology and adhesion of Bi films through electroplating,[6,7] probably due to the instability of free Bi^{3+} ions in aqueous media. Based on the above considerations, this work tries to control the preferred orientation ratio (denoted as *f*), Bi(110)/Bi(012) facets, of Bi deposits through electroplating.

Due to the complicated influences of preparation variables on the preferred orientation ratio of bismuth deposits and the challenge in electroplating of bismuth films with good qualities (e.g., uniformity, good adhesion, etc.), this work employed the fractional factorial design (FFD) to screen out the key factors affecting the textures of Bi deposits significantly, which include pH, current density, concentration of polyethylene glycol (PEG, MW400), bath temperature, and stirring rate. Then, using the path of the steepest descent/ascent (PSD/PSA) study to extend and control the preferred orientation ratio of Bi deposits for future applications.

Experimental

Bismuth deposits were electroplated from a solution containing 0.06 M $Bi(NO_3)_3 \cdot 5H_2O$ (Hayashi, EP), 0.3 M citric acid (CA, Shimakyu, EP), 4000 ppm gelatin (from porcine skin, Type A ∼ 300 Bloom (G2500-100G)), 0.3 M ethylenediaminetetraacetic acid (EDTA, Riedel-deHaen, GA), and variable concentrations of polyethylene glycol (PEG, MW400, Shimakyu, EP) onto copper (99.5%, 1.094×10^{-2} cm^2, 1.18×10^{-1} cm in diameter) circular plates which have been deposited with a nickel film (ca. 2 μm). The pretreatment procedures of Cu/Ni substrates completely followed our previous work.[12–14] The Cu/Ni substrates, rinsed with deionized water, were placed in a 50-mL jacket cell and faced with a dimensionally stable anode (DSA) to electroplate Bi deposits. The dimensions of the stirring bar are 1.5 cm in length and 6mm in diameter. The dimensions of 50-mL jacket cell are 4.5 cm in diameter and 4 cm in height. The pH of plating baths was adjusted with concentrated HCl or NH_4OH. After deposition, these electrodes were repeatedly rinsed with deionized water and finally dried in a vacuum oven at room temperature.

Morphologies of all deposits were examined by a field emission scanning electron microscope (FE-SEM, Hitachi S-4700). X-ray diffraction patterns were obtained from an X-ray diffractometer (CuK$_\alpha$, Ultima IV, Rigaku). All solutions were prepared with deionized water produced by a reagent water system (Milli-Q SP, Japan) at 18 MΩ cm and all reagents not specified were Merck, GR. Solution temperature was maintained at the specified temperature with an accuracy of 0.1°C by means of a water thermostat (Haake DC3 and K20).

Results and Discussion

Fractional factorial design.— For this complicated electroplating system, the fractional factorial design (FFD) is used to efficiently screen out the key variables affecting the preferred orientation ratio, *f*, of Bi deposits. The main advantage of FFD is that the quantitative effects of electroplating parameters can be efficiently assessed by means of limited experiments. Another merit of FFD is the observation of the influence of each variable at a variety of other variable levels as well as the interactions among these variables on the response variable (i.e., the intensity ratio of Bi(110)/Bi(012) facets, *f*, in this work). The preferred orientation ratio, *f*, is defined as follow:

$$f = \frac{Bi(110)}{Bi(012)} = \frac{I_{39.7^\circ}}{I_{27.3^\circ}} \qquad [1]$$

where *I* indicates the intensity of X-ray diffraction peak.

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Table I. Factors and levels for the 2^{5-1} fractional factorial design.

Factor	Level −	Level +
A. pH	4	6
B. Current density (mA cm^{-2})	3	30
C. PEG concentration (mM)	20	100
D. Temperature (°C)	25	50
E. Stirring rate (rpm)	80	160

There are five electroplating variables in the FFD study: (A) pH, (B) current density (mA cm^{-2}), (C) concentration of PEG (M), (D) temperature (°C), and (E) stirring rate (rpm). In general, the selection for the factor levels needs brain-storming which includes literature review, previous experiences, and some preliminary tests in order to obtain useful information.[24–26] For example, the low and high levels of pH in the plating baths are equal to 4 and 6, respectively, because the EDTA solubility decreases with decreasing pH while $Bi(OH)^{2+}$ ions will be formed when the pH value is higher than 6,[2] which is hard to be deposited. In addition, according to our previous work for factors B and C,[23] to suppress the dendrite formation and to make excellent crystalline quality of Bi films, the current density is set at 3 and 30 mA cm^{-2} for low and high levels of factor B meanwhile 20 and 100 mM of PEG are selected as the low and high levels of factor C because PEG is a strong additive adsorbing on the Bi surface to inhibit the Bi dendrite formation. Moreover, due to the possible formation of hydrogen bonds among PEG and water molecules, the possible interaction effect between PEG and temperature has to be considered since the hydrogen bonds between PEG and H_2O molecules are expected to be broken significantly at higher bath temperatures due to the more significantly thermal motions of PEG and water molecules. Hence, the low and high levels of the bath temperature are set at 25 and 50°C, respectively. The hydrodynamic situation, controlled by the stirring rate of magnetic bars, generally affects the diffusion of metallic ions and the growth rate of bismuth crystals, resulting in the setting for the high and low levels of the stirring rate equal to 160 and 80 rpm, respectively. The fixed levels of these five variables are listed in Table I meanwhile a 2^{5-1} design matrix with the experimental data is given in Table II.

Table II. The design matrix and the *f* value of Bi deposits for the 2^{5-1} fractional factorial design with the defining relation I = ABCDE.

Run	Factors A	B	C	D	E	*f*
1	−	−	−	−	+	0.484
2	+	−	−	−	−	0.344
3	−	+	−	−	−	0.617
4	+	+	−	−	+	0.337
5	−	−	−	−	−	0.571
6	+	−	+	−	+	0.337
7	−	+	+	−	+	0.482
8	+	+	+	−	−	0.309
9	−	−	−	+	−	0.398
10	+	−	−	+	+	0.070
11	−	+	−	+	+	0.113
12	+	+	−	+	−	0.383
13	−	−	+	+	+	0.093
14	+	−	+	+	−	0.021
15	−	+	+	+	−	0.136
16	+	+	+	+	+	0.446

A 2^{k-1} FFD matrix can be constructed by writing down a basic design matrix consisting of a full 2^{k-1} factorial design and then adding the kth factor by identifying its contrast coefficients from the plus and minus signs of the highest-order interaction ABC… (K-1). For example, a 2^{5-1} design with the defining relation, I = ABCDE (introduced by Box et al.[24]), shows the following property.

$$E = E \cdot I = E \cdot ABCDE = ABCDE^2 = ABCD \qquad [2]$$

Therefore, the 2^{5-1} design can be obtained by writing down a full 2^4 orthogonal array as the basic design and then equating factor E to the ABCD interaction.[25] In Table II, the low and high levels of A, B, C, D, and E were denoted as "−" and "+", respectively. The contrast coefficients of factor E (i.e., column 6 in Table II) is generated from the contrast coefficients of factors A, B, C, and D according to Eq. 2. Thus, the orthogonal contrast coefficients of factor E are equal to that of its alias, the four-factor interaction of A (pH), B (current density), C (PEG concentration), and D (bath temperature). As a result, the observations used to estimate the effect of factor E (stirring rate) are identical to those used to estimate the four-factor interaction effect. Hence, the effects of factor E and ABCD interaction are said to be confounded and indistinguishable.[25,26] From the sparsity of effects principle,[25] however, a system is likely to be driven primarily by the effects of certain main factors and low-order interactions. Therefore, effects of high-order (e.g., three and higher order) interactions are generally assumed to be negligible and the effect of factor E can be isolated from the confounded effects (resolution = V).[25]

From an examination of the results in Table II, *f* varied from 0.021 to 0.617, indicating that certain factors and/or interactions show significant effects on the preferred orientation ratio of Bi deposits. Accordingly, analysis of variance (ANOVA) for the data in Table II was performed, which is summarized in Table III. ANOVA is derived from partitioning the sum of squares of total variances (*SST*) into its component parts (i.e., sums of square for model and error, SS_{model} and *SSE*, respectively), which can be calculated on the basis of the following equations:[27]

$$SST = \sum_{i=1}^{2^{k-1}} (y_i - \bar{y})^2 \qquad [3]$$

$$SS_i = \frac{(C_i)^2}{2^{k-1}} \qquad [4]$$

$$SSE = SST - SS_{\text{model}} \qquad [5]$$

where y_i and $\bar{y}$ are indicative of the *i*th response and the grand average of all the observations, respectively. Note that C_i is indicative of the contrast of factor (or interaction) *i*, which is the sum of multiplying

Table III. Analysis of variance for the *f* value of the Bi deposits from the 2^{5-1} fractional factorial design.

Source	SS	d.f.	MS	*F* [a]
A	0.028	1	0.028	7.065
B	0.017	1	0.017	4.354
D	0.211	1	0.211	53.418
E	0.010	1	0.010	2.474
AB	0.053	1	0.053	13.411
AD	0.061	1	0.061	15.357
AE	0.031	1	0.031	7.783
BD	0.016	1	0.016	4.048
ABD	0.073	1	0.073	18.406
Error	0.024	6	0.004	
Total	0.523	15		

[a] *Remark*: $F_{0.05}(1,6) = 5.99$; $R^2 = 0.955$.

the observations (i.e., y_i) with the appropriate contrast coefficients (i.e., the plus-minus signs in an appropriate column of the design matrix). For example, the contrast of factor A is expressed as: $C_A = -y_1 + y_2 - y_3 + y_4 - y_5 + y_6 - y_7 + y_8 - y_9 + y_{10} - y_{11} + y_{12} - y_{13} + y_{14} - y_{15} + y_{16} = -0.647$. In addition, SS_i indicates the sum of square corresponding to factor (or interaction) i. The sum of SS_i with statistical significance is defined as SS_{model}. The quantities $MS_i = SS_i/df_i$ and $MSE = SSE/df_{error}$ are defined as the mean squares of factor (or interaction) i and the mean square of error, respectively. The df_i and df_{error} indicate the degree of freedom for factor (or interaction) i and error, respectively. In Table III, the test statistics, F^*, defined as MS_i/MSE, are employed to test the statistical significance of each factor or interaction. If the calculated value of F^* is greater than that in the F table at a specific probability level (e.g., $\alpha = 0.05$), a statistically significant factor or interaction is obtained. After the test, factors A, B, D as well as interactions AB, AD, AE, BD, and ABD show significant effects on the preferred orientation ratio of Bi deposits. Note that factor E is considered as a factor with marginal significance (i.e., its effects is not as important as the effects of factors A, B, D, and interactions AB, AD, AE, BD and ABD) because its calculated F^* value is somewhat lower than the critical value ($F_{0.05}$ (1, 6) = 5.99). However, according to the hierarchical principle,[24] if a model contains a high-order term (such as AE in this work), it should also contain all of the lower-order terms that composite it (i.e., factor E in this case). Therefore, the model obtained from the ANOVA contains factor E. Also note that interaction ABD (but not interaction CE) is also considered here because significant factors easily lead to significant interactions.[25] The multiple correlation coefficient, $R^2 = 1-(SSE/SST)$, is the proportion of SST (sum of squares of total variances) explained by the fitted equation. A R^2 value close to 1 means a good fit to the experiment data. In this work, $R^2 = 0.955$ indicates an excellent fitting when factors A, B, D, and E as well as interactions AB, AD, AE, BD, and ABD are considered to be significant. The other effects (including factor C and the other interactions) were pooled into the error.

Calculation of the effect estimates for factors and interactions followed the procedure recommended by Box et al.,[24] which is equal to $C_i/2^{k-2}$. The effect estimates of factors A–E and interactions with statistical significance are shown in Figure 1. From Table III and Figure 1, it is very clear that the sequence of factors/interactions with respect to decreasing the influence is: D > ABD > AD > AB > AE >A > B > BD > E. Based on the results of Table III and Figure 1a, changing the temperature of the plating solution (factor D) from 50 to 25°C obviously increases the f value from 0.2 to 0.43. In addition, the low level of factors A (pH = 4) and E (stirring rate = 80 rpm) as well as the high level of factor B (current density = 30 mA cm^{-2}) can be used to increase the preferred orientation ratio of Bi deposits. Since factor C (PEG concentration) is not significant here, the difference in the f value between the high and low levels of this factor is considered as an error, probably due to that the PEG concentration at the low level (20 mM) is high enough. From all the above results and discussion, the preferred orientation ratio of Bi deposits is strongly affected by varying the plating temperature but is weakly dependent on the pH value, current density, and stirring rate.

The significant influences of AB, AD, AE, BD, and ABD interactions on the f value of Bi deposits are shown in Figure 1b. From this figure, a decrease in pH of the plating solution (Factor A) leads to an obvious increase in the f value of the deposits when the current density of electroplating (factor B) is under the low level (3 mA cm^{-2}). However, when this factor is under the high level (30 mA cm^{-2}), the pH effect becomes insignificant. The above phenomena reveal the existence of an interaction between factors A and B, while a deposit with a higher f value will be obtained when it is plated at a lower current density in a more acidic solution. Fortunately, from Table III, factor B is a relatively minor factor in comparing with the effect of interaction AB although this factor in the high level slightly increases the f value of the deposits (see Fig. 1a). For interaction AD, a deposit with a higher f value will be obtained when it is plated at a lower temperature in a more acidic solution. This trend is consistent with the main effects of factors A and D. A similar phenomenon is also found for interaction AE (i.e., a higher f value is obtained for the deposits prepared from a low level of factor E and a low level of factor A). The ABD interaction shows that when interaction AB is under the low level, an increase in the f value will be obtained when factor D is moved from the high level to the low level. For BD interaction, the influence of factor D on the f value is more obvious when factor B is under the low level in comparison with that as factor B is under the high level. Moreover, decreasing the temperature and pH of the plating bath (factors A and D) always promotes the f value of deposits despite the levels of factors B and E. This result indicates the monotonous influences of factors A and D on the f value in this electroplating system, which can be employed as the reliable variables for controlling the preferred orientation ratio of Bi deposits.

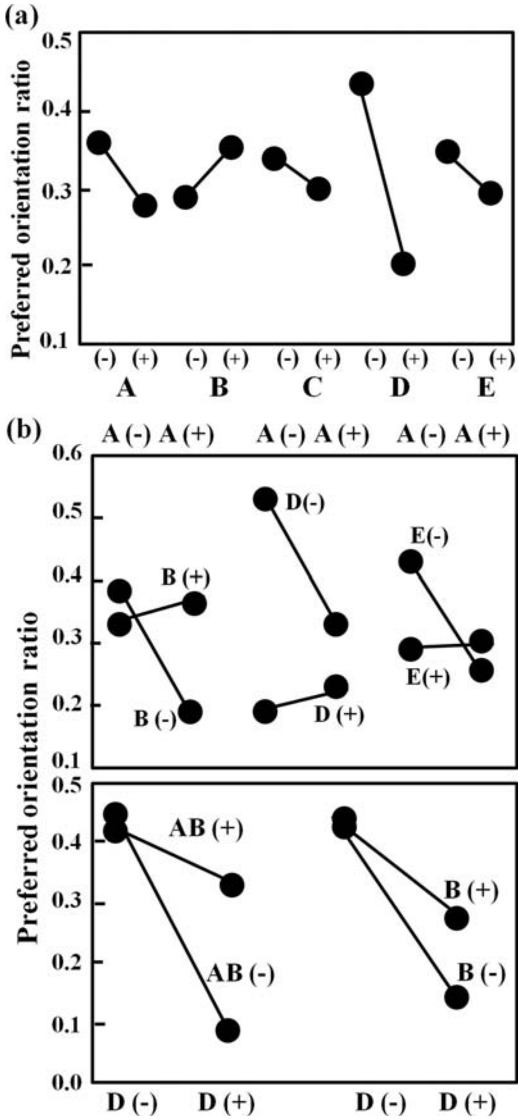

Figure 1. Effects of (a) factors (A) pH, (B) current density (mA cm^{-2}), (C) PEG concentration (mM), (D) temperature of the plating bath (°C), and (E) stirring rate (rpm) and (b) interactions AB, AD, AE, ABD, and BD on the f value of Bi deposits, where (+) and (−) indicate the high and low levels of factors/interaction, respectively.

From the regression analysis of the results in Table II, a fitted polynomial model (including the marginal effect) can be generated. This model, quantitatively elucidating the effects of all factors and interactions with statistical significance, is expressed as follow:

$$f = 0.321 - 0.040x_A + 0.032\,x_B - 0.114\,x_D - 0.026\,x_E + 0.056\,x_Ax_B + 0.063\,x_Ax_D + 0.043\,x_Ax_E + 0.030\,x_Bx_D + 0.066\,x_Ax_B\,x_D \quad [6]$$

where x_i are the coded variables for factor i (i.e., A, B, D, and E). The coded variables, x_i, are defined in the standardized form as following:[25]

$$x_{i,HIGH} = (X_{i,\text{HIGH}} - X_{i,\text{MEAN}})/S_i \quad (=+1) \quad [7]$$

$$x_{i,LOW} = (X_{i,\text{LOW}} - X_{i,\text{MEAN}})/S_i \quad (=-1) \quad [8]$$

$$X_{i,MEAN} = (X_{i,\text{HIGH}} + X_{i,\text{LOW}})/2 \quad [9]$$

$$S_i = (X_{i,\text{HIGH}} - X_{i,\text{LOW}})/2 \quad [10]$$

where $X_{i,\text{HIGH}}$ and $X_{i,\text{LOW}}$ are the high and low levels of factor i in the natural unit, respectively. Eq. 6 is a function of factors A, B, D, and E, which shows that the *f* value of deposits will increase with decreasing temperature (factor D) since the coefficient of factor D is negative (−0.114). Moreover, the influence of factor D is the highest among all factors and interactions because the absolute value of its coefficient is the largest.

Path of the steepest descent/ascent study.— Based on Eq. 6, a study for the path of the steepest descent/ascent (PSD/PSA) and the corresponding results are shown in Table IV. The starting point (run 3) is set at the origin of factors A and D (i.e., $x_A = 0$ and $x_D = 0$). To extend the preferred orientation ratio of Bi deposits, factors A and D were varied simultaneously with the regular step sizes of factors A and D equal to 0.5 (in pH) and 6.25°C (in plating temperature), respectively. The upper limits of factors A and D (i.e., run 1) are set at the extreme plating condition for obtaining a deposit with the lowest *f* (i.e., pH = 6.0 and plating temperature = 50°C). The variation in *f* with factors A and D is very obvious and almost constant when pH and temperature of the plating bath are respectively ranged from 6.0 to 4.5 and from 50 to 31.3°C. This result reveals the reliability of ANOVA in the FFD study. Note here that in order to obtain the lowest *f* value, the direction of the PSD study was slightly modified (i.e., runs 1 and 2); i.e., the concentration of PEG was increased from 20 to 100 mM. Since the adhesion of Bi deposits becomes poor and cracks are visible at temperatures equal to/lower than 25°C, the bath temperature of 28.1°C and pH of 4.25 are recommended as the lowest limits of factors D and A, respectively. According to the above consideration, the step sizes of factors A and D are reduced. Clearly, a deposit with the highest *f* value is obtained under the plating condition of run 4. Based on the results shown in Table IV, the preferred orientation ratio of Bi(110)/Bi(012) facets for Bi deposits can be simply controlled by varying the pH value, plating temperature, and PEG concentration from a simple plating bath basically containing 0.06 M $Bi(NO_3)_3 \cdot 5H_2O$, 0.3 M citric acid, 4000 ppm gelatin, and 0.3 M EDTA under a constant current density (3 mA cm^{-2}).

Table IV. Dependence of the *f* value of Bi deposits on pH (factor A) and temperature (factor D) of the plating bath in the PSD/PSA study.

	Factor		
Run	A	D	*f*
1[a]	6.0	50	0.01
2[a]	5.5	43.8	0.56
3[b]	5.0	37.5	0.82
4[b]	4.5	31.3	1.32
5[b]	4.25	28.1	0.89

[a] Factors B, C, and E are 3 mA cm^{-2}, 100 mM, and 80 rpm, respectively.

[b] Factors B, C, and E are 3 mA cm^{-2}, 20 mM, and 80 rpm, respectively.

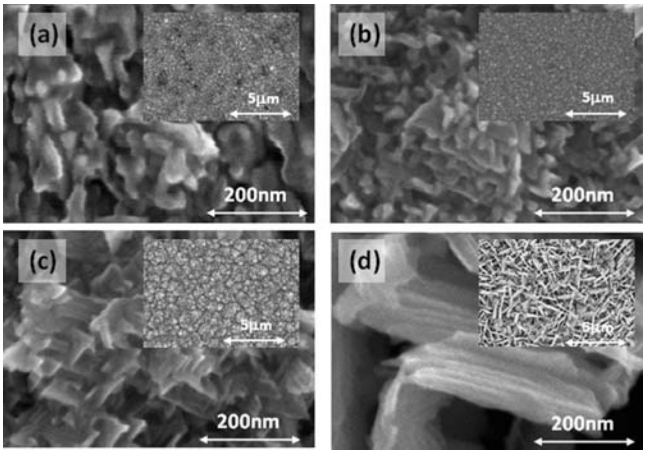

Figure 2. The FE-SEM photographs of Bi deposits with the *f* value of (a) 1.32, (b) 0.82, (c) 0.56, and (d) 0.01.

Morphology of Bi deposits with different f values.— The morphologies of Bi deposits with the *f* value varying from 1.32 to 0.01 are shown in Fig. 2. The insets show the morphologies under a lower magnification. From all insets in Fig. 2, all deposits show uniform morphologies while the deposit with the lowest *f* value (Fig. 2d) seems to be obviously rougher in comparison with the other deposits. In Fig. 2a, irregular/ellipsoid-like particles between 50 and 100 nm are visible although the particle boundaries are not very clear. With decreasing the *f* value, the particles transform into irregular/triangular platelets (see Fig. 2b). In Fig. 2c, piling triangular platelets up into aggregates is visible and sharp edges of crystallites are clearly found. The piling of metallic rods is very clear in Fig. 2d, resulting in the formation of many prickly rods with length longer than 600 nm on this deposit (see inset). All the above results indicate that controlling the preferred orientation ratio of Bi deposits leads the simultaneous change in the surface morphology of Bi deposits. The influences of the preferred orientation ratio of Bi deposits on the sensing ability of heavy metal ions will be systematically investigated in our next study.

Conclusions

From the FFD study, the preferred orientation ratio of Bi(110)/Bi(012) facets, *f*, on Bi deposits is strongly affected by the plating temperature but only weakly depends on the pH value, current density, and stirring rate. Moreover, from the analyzes of significant interaction effects, factors A and D exhibit monotonous influences on the *f* value in electroplating Bi deposits, which can be employed as the reliable variables for controlling the preferred orientation ratio of Bi deposits. This idea has been confirmed in the path of the steepest descent/ascent study and the preferred orientation ratio of Bi(110)/Bi(012) facets from 1.32 to 0.01 can be simply controlled by varying the pH value, plating temperature and PEG400 from a simple plating bath basically containing 0.06 M $Bi(NO_3)_3 \cdot 5H_2O$, 0.3 M citric acid, 4000 ppm gelatin, and 0.3 M EDTA.

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