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Tip current/positioning close-loop mode of scanning electrochemical microscopy for electrochemical micromachining

Lianhuan Han[a,b], Xuesen Zhao[b], Zhenjiang Hu[b], Jie Zhang[c,d], Yongzhi Cao[b], Yongda Yan[a,b,*], Zhong-Qun Tian[c,d], Zhao-Wu Tian[c,d], Dongping Zhan[c,d,**]

[a] *Key Laboratory of Micro-Systems and Micro-Structures Manufacturing of Ministry of Education, Harbin Institute of Technology, Harbin, Heilongjiang 150001, China*
[b] *Center for Precision Engineering, Harbin Institute of Technology, P.O. Box 413, Harbin 150001, China*
[c] *State Key Laboratory of Physical Chemistry of Solid Surfaces (PCOSS), Collaborative Innovation Centre of Chemistry for Energy Materials (iChEM), Xiamen 361005, China*
[d] *Department of Chemistry, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, China*

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ABSTRACT

Scanning electrochemical microscopy (SECM) has been approved as a prospective electrochemical micromachining (ECMM) technique soon after its birth. However, it still remains challenge for SECM to fabricate arbitrary three-dimensional (3D) microstructures because of the limitation of positioning system. To solve this problem, we proposed a tip current signal/positioning close-loop mode in which the tip current signal is fed back to the positioning system in order to program the motion trial of SECM tip. Both the triedge-cone and sinusoidal microstructures were obtained by the close-loop positioning mode. The static-state etching process was demonstrated not to be disturbed by the slow motion rate of SECM tip. The unique positioning mode would be significant for both ECMM and electrochemical imaging.

1. Introduction

SECM has been proved a powerful scanning probe microscopy (SPM) applicable to all electrochemical domains from the electrode kinetics through the single entities to micropatterning and micromachining [1–5]. Similar to the other SPM techniques, positioning system is the key part of SECM instrument. At beginning, the tunnel current [6], atomic force [7], shear force [8] and ion conductance [9,10] were adopted as the feedback signals for SECM tip positioning [11]. However, the tip preparation still remains great challenges [12–14]. Although constant tip current was adopted as the feedback signal for the constant-distance scanning mode, it applies only to the inert or homogeneous active substrate [15,16]. Usually, the commercial SECM workstation works with the constant-height scanning mode because no communication is needed between the positioning system and the electrochemical signals. Thus, it is important to develop new positioning mode to program the motion trail of SECM tip in order to broaden the application of SECM in electrochemical investigations.

ECMM takes the advantages of no tool wear, no residual strains, no surface and subsurface damages, high efficient and low cost [17–19]. Soon after the birth of SECM, great efforts have been made to develop it as a direct-writing ECMM technique through electrodeposition, electrolysis and the subsequent etching reactions [20–25]. Most of the studies were performed with a constant-height mode [26–29]. Thus, it is difficult for SECM to fabricate the complex 3D microstructures with arbitrary profiles. To overcome this problem, here we developed a close-loop feedback mechanism between the tip current signal and tip positioning, by which the motion trial of the SECM tip can be programmed and the corresponding 3D microstructures can be obtained on n-GaAs substrate as expected.

2. Experimental section

2.1. Chemicals and materials

The chemicals, NaBr and H_2SO_4, are analytical grade provided by Sinopharm Co., China. Silicon doped n-type GaAs (100) wafers (n-GaAs) with doping level between (0.8–2.3) × 10^{18} cm^{-3} were purchased from Chinese Crystal Technologies Co., China. The n-GaAs substrate was cleaned with acetone and deionized water for several times before use. The aqueous solution was prepared with deionized water (18.2 MΩ cm, Milli-Q, Millipore Co.).

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[*] Correspondence to: Key Laboratory of Micro-Systems and Micro-Structures Manufacturing of Ministry of Education, Harbin Institute of Technology, Harbin, Heilongjiang 150001, China.
[**] Correspondence to: Department of Chemistry, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, China
E-mail addresses: yanyongda@hit.edu.cn (Y. Yan), dpzhan@xmu.edu.cn (D. Zhan).

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2.2. Instruments and measurements

A home-made SECM/ECMM instrument was employed in our experiments as reported previously [25]. A 100-μm-diameter Pt disk electrode was well polished to a RG value of 2 and characterized by an optical microscopy (BX-51, Olympus, Japan) and steady-state voltammetry [30]. A Pt wire was adopted as the counter electrode and a saturated Ag/AgCl electrode was adopted as the reference electrode. In the static-state machining experiment, the tip was fixed at a series of distance above the n-GaAs substrate and held at constant potential of 1.2 V in a solution containing 100 mM NaBr and 0.5 M H_2SO_4. The positioning details of the dynamic machining experiments is described as followed, and the other conditions are the same as static-state machining.

As for the n-GaAs substrate, a positive current feedback curve can be obtained to calibrate the initial current at a chosen tip-substrate distance. The contact point was determined by a force sensor (FSH02664, FUTEK Advanced Sensor Technology Inc., USA) when the Pt tip touches the n-GaAs substrate with a contact force of 0.5 mN. Before the machining experiments with the scanning mode, the Pt tip was withdrew back a certain distance above the n-GaAs substrate and held at a constant potential of 1.2 V. As shown in Fig. 1a, the tip current response was fed back and compared with the tuned current signal (e.g., the sinusoidal wave). The difference between them (or, current error) was input to the PZT controller through a PID controller. Thus, the tip would move in the Z-direction as expected to adjust the tip-substrate distance. The tuned current signal, 2D tip trajectory in Z-direction and the 3D tip trajectory are shown in Fig. 1b.

The profiles and images of the obtained 3D microstructures were characterized by a home-made scanning force microscopy (SFM) integrated in our SECM/ECMM instrument, where a diamond cone (tip diameter: 10 μm) was adopted as the scanning tip and the contact force is held constant at 2 mN. Considering the surface passivation, a finite element simulation was performed by Comsol Multiphysics where a calibration factor (γ) was introduced in Eq. (16) of the model proposed in our previous work ($v_z = -\gamma k_{sub} C_{Br^2} / \rho_{GaAs} \nu_{Br^2}$) [31,32].

3. Results and discussions

We have studied the reaction kinetics and the surface passivation effect of the confined etching system for III-V group semiconductors. Considering the surface passivation effect on the etching processes, we performed the static-state machining experiment where the SECM tip is fixed at a series of distance above the n-GaAs substrate. The profiles of the obtained pits with 100-seconds' etching were shown in Fig. 2a. Here we introduce a calibration factor (γ) in the finite element analysis. By using the kinetic rate of n-GaAs etched by electrogenerated Br_2 (3.2×10^{-2} cm s^{-1}) obtained previously, γ is obtained as 0.67 which indicates that the passivation effect cannot be neglected during the long-time etching process. To figure out the correlation between the current response and the etching depth, the tip current at static state was normalized by that obtained in the buck solution ($I_{tip} = i_e / i_\infty$). The results showed that both the normalized tip current and etching depth decreased with the increasing tip-substrate distance (Fig. 2b). And the normalized tip current and etching depth presented a linear relationship with a slope of 0.48 μm/μA, indicating that the local etching rate was tunable by controlling both the tip-substrate distance and the current applied to the SECM tip. Thus, it would be possible to fabricate arbitrary 3D microstructures if the tip current were fed back to the positioning system.

A triangle-wave current was adopted as the tuned signal, the difference of which from the tip current was fed back to the positioning system. To avoid the scratch of the SECM tip on the n-GaAs substrate, the maximum current was fixed at the steady-state current (9.84 μA) obtained at the tip-substrate distance of 10 μm. The minimum current and the period were set as 5.38 μA and 500 s. The motion rate and travel distance were set as 10 μm/s and 1.5 mm. Consequently, a triedge-cone microstructure was obtained on n-GaAs surface as shown in Fig. 3a. The maximum and the minimum etching depths were measured by SFM as 3.25 μm and 1.55 μm. The period of the triedge-cone microstructure was 0.505 mm, which was in harmonious with the product of the period of the triangle-wave current and the motion rate (i.e., 0.5 mm). It was found from Fig. 3b that the etching depth and the applied triangle-wave current abided by the empirical equation$z(\mu m) = 0.431 i(\mu A) - 0.909$ (Fig. 3c). The slope is very close to that obtained in the static-state machining experiment, indicating that the slow motion rate (10 μm/s) had little effect on the mass transfer in the tip-substrate gap and, thus, the local etching process therein. In other words, the etching process is in a static state when the SECM tip is moving with a rate of 10 μm/s.

Furthermore, a sinusoidal current was adopted to fabricate a sinusoidal surface. The current applied to the SECM tip was set as $i(x,y) = \alpha A \sin(2\pi x/500)\sin(2\pi y/500) + i_0$ and fed back to the positioning system to program the motion trail of the SECM tip, where α and i_0, were the current-etching depth ratio and the reference current, respectively. The motion rate was set as 10 μm/s and the travel distance were 1 mm in the X and Y directions. From the results of static-state etching process, the maximum and the minimum etching depths were expected as 3.30 μm and 1.37 μm. The obtained sinusoidal 3D surface (Fig. 4a) showed that the maximum and the minimum etching depths were 3.38 μm and 1.68 μm, indicating the machining resolution of 0.08 μm and 0.31 μm. Moreover, the SFM profiles and the applied sinusoidal current had the same period (Fig. 4b and c). All the results elucidated further that the etching process is in the static state with the slow motion rate of 10 μm/s.

The local etching rate and the machining accuracy are affected by the multi-factors such as the kinetic properties of the etching system, tip size, the applied potential or current, the tip-substrate distance, the electrolyte components, the tip motion rate, etc. When the tip current was fed back to the positioning system, the tip would move in the Z direction and change the tip-substrate distance. It should be noted that, as shown in Fig. 1b, the tip trail is not the same as the waveform of the

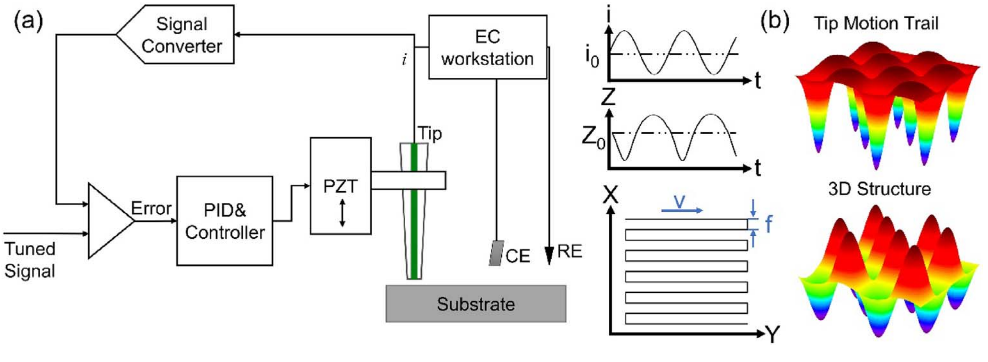

Fig. 1. (a) Schematic diagram of the tip current/positioning close-loop mode of SECM for electrochemical micromachining. The tip current signal is close-looped to the positioning system to control the tip motion trail in Z direction. The CE and RE refers to the counter electrode and the reference electrode. The motion rate (v) and the feeding distance (f) were set as 10 μm/s and 10 μm. (b) The motion trail of SECM tip and the expected 3D microstructure.