seems more convenient to use a tip of needle shape, just as the one used in STM. Since the feedback current used to control d_{t-s} in SECM will be less sensitive to the distance changes of the needle-shaped tip, an electrochemical scanning tunneling microscopy (ECSTM) system may be used to direct the tip movement and to control the tip-substrate separation. Work aiming at this goal is currently in progress.

Key words Confined etchant layer technique (CELT), Silicon, High resolution etching

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利用约束刻蚀剂层技术提高硅的刻蚀分辨率

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摘要 高分辨率刻蚀技术对于微机械及微电子器件的加工具有十分重要的意义,而硅是其中极为重要并占统制地位的材料。近年来,扫描电化学显微镜(SECM)用于表面加工的研究颇受注目。然而,SECM 刻蚀分辨率往往因为刻蚀剂的横向扩散而受到限制。最近,田昭武等提出的一种可进行高分辨率微加工的新方法——约束刻蚀剂层技术(CELT),可使刻蚀反应具有高度的距离敏感性,刻蚀分辨率得到极大改善。我们利用 CELT 技术刻蚀硅表面,以 60 μm 及 100 μm 直径微电极产生刻蚀剂 Br_2,刻蚀溶液中加入亚砷酸作为 Br_2 的捕捉剂刻蚀得到的图案与所用微电极尺寸符合,直径分别约为 60 μm 和 100 μm。与 SECM 方法得到的 110 μm 和 180 μm 分辨率相比,刻蚀分辨率得到大幅度提高。

关键词 约束刻蚀剂层技术(CELT),硅,高分辨率刻蚀

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Improved Etching Resolution on Silicon by the Confined Etchant Layer Technique①

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Micro- and nano-fabrication techniques are of great importance in miniaturizing man-made systems. The scanning electrochemical microscopy (SECM) has been introduced recently as a very promising wet etching technique for modifying metal and semiconductor surfaces[1~3]. However, the highest achievable resolution of etched patterns on the surface by SECM depends not only on the tip diameter from which etching species are generated but also the radial diffusion of the etchant under the SECM configuration. It has been shown that etching process takes place on surfaces such as GaP, CdTe and Si in a much larger area than the actual tip diameters[2,3]. Obviously, this limitation of SECM due to the diffusion of etchant hampers its applicability in high resolution fabrication of surfaces.

However, a confined etchant layer technique (CELT) recently proposed by Tian et al. overcome the problems by confining the etchant to a certain distance from the tip where it is generated. Furthermore, the principle of CELT will also lead to a new electrochemical wet etching technique for real three-dimensional replication with high resolution[4,5].

In the etching process using CELT, the active etchant generated at an electrode surface can be rapidly consumed through homogeneous reaction with other redox couples on its way of diffusing to the substrate. Thus, the etchant can be confined within a very thin diffusion layer surrounding the tip electrode surface, and a replication of 3D pattern with high resolution can be realized. The thickness of the confined etchant layer (CEL) can be represented by the specific thickness of the diffusion layer (μ), which is given by[4]

$$\mu = (D / k_s)^{1/2} \quad (1)$$

where D is the diffusion coefficient of etchant in solution, and k_s is the rate constant of the pseudo-first-order scavenging reaction.

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In this letter, we report work on improved etching resolution on Si by CELT. CELT experiments were conducted with a controlled micropositioning device assembled in our laboratories. For comparison, the experiments were first conducted based on the SECM etching principle in a solution of 5 mmol · dm^{-3} HBr, 0.5 mol · dm^{-3} HF and 0.5 mol · dm^{-3} H_2SO_4. CELT etching experiments were then conducted in a different place and in the same solution with the addition of 50 mmol · dm^{-3} H_3AsO_3 as the scavenger for bromine generated at the microelectrode.

Results and Discussions

In the SECM etching process, a positive feedback current appeared as the tip approaches the silicon surface. The SECM feedback mechanism was extensively studied by Bard and co-workers. The positive feedback current observed in this experiment was the result of the bromine recycling between the tip and the substrate. The electron transfer between bromine

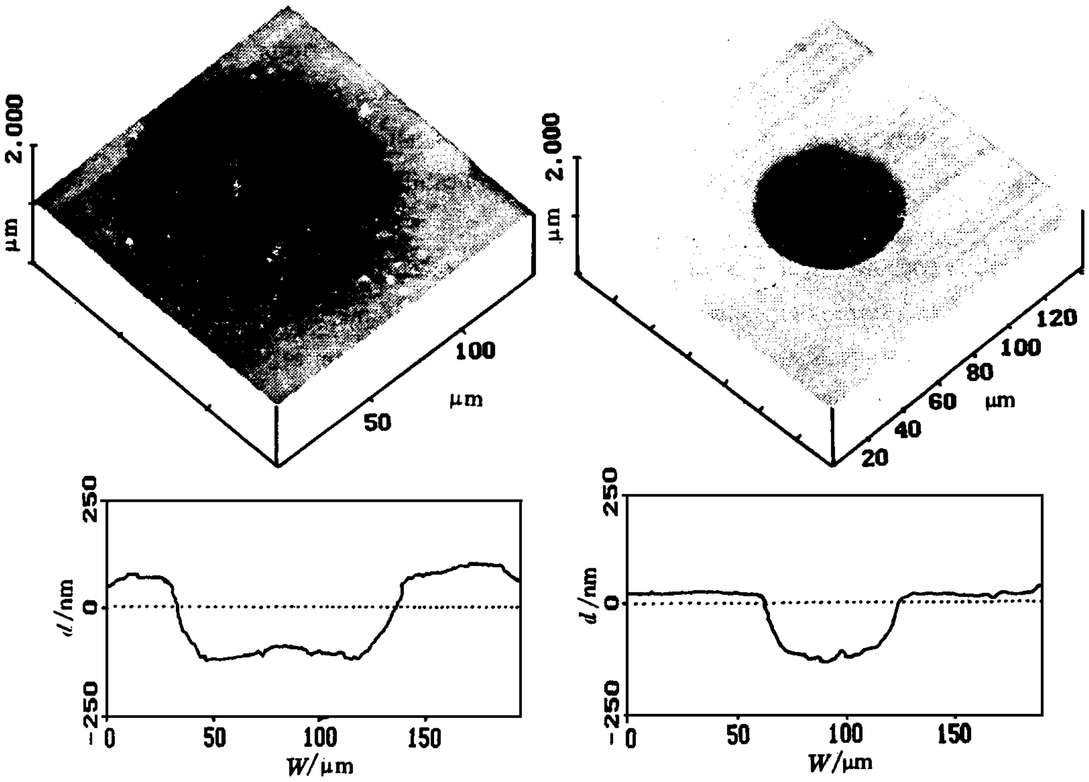

Fig. 1 AFM surface plot and section analysis of an n-type Si<111> surface etched with a 60 μm diameter platinum microelectrode (a) for 10 min in a solution of 5 mmol · dm^{-3} HBr, 0.5 mol · dm^{-3} H_2SO_4 and 0.5 mol · dm^{-3} HF, and (b) for 20 min in above solution with the addition of 50 mmol · dm^{-3} H_3AsO_3

species and silicon leads to the etching at the silicon surface. Fig. 1 is the AFM surface plot and section analysis of a typical etching spot on Si surface obtained after etching using the platinum microelectrode of 60 μm in diameter. The outer size of the etching pattern is about 110 μm, almost doubled that of the microelectrode diameter. This result indicates that the etching resolution is not determined by the size of the tip only. For the etching process where the heterogeneous electron transfer is not fast enough, the etching resolution can be even more seriously lowered due to the thick radial diffusion layer of the etchant.

In the etching process based on CELT, a scavenger chemical of H_3AsO_3 was added into the electrolyte solution to consume the etchant rapidly and homogeneously. The etching resolution will dominantly depend on the rate of the scavenge reaction of bromine. High lateral resolution of the etching pattern is expected for a large reaction rate constant (k_s). The homogeneous bromine consuming reaction is as follows:

$$Br_2 + H_3AsO_3 + H_2O \rightarrow 2Br^- + H_3AsO_4 + 2H^+ \qquad (2)$$

The second-order rate constant of reaction (2) in sulfuric acid has been determined to be around 3.6×10^5 L·mol^{-1}·s^{-1}[6]. The pseudo-first-order reaction rate constant k_s is about 1.8×10^4 s^{-1}. The thickness of confined bromine layer can be calculated from equation (1) with the result of about 0.25 μm. The bromide species oxidized at microelectrode surface regenerated rapidly due to the homogeneous reaction (2), and consequently, even when the tip was far from the substrate, the tip current was several times larger than that absent of H_3AsO_3. As the microelectrode approaches the substrate to within several hundreds of nanometers, a much smaller positive feedback current appeared than in oridnary SECM experiments and the etching reaction took place.

The etching result obtained with the 60 μm-diameter platinum microelectrode with CELT is presented in Fig. 1b. The upper limit of the width of the etched spot with clear "cut off" edge is around 60 μm, matching precisely the microelectrode diameter. The high etching resolution gives an evidence for the effective confinement of the diffusion layer of etchant. The silicon surface not right beneath the tip survived, therefore, from the attack of short-life bromine species. A 100 μm-diameter platinum electrode has also been used for silicon etching, and the diameters of etching patterns obtained with and without using CELT are about 100 μm and 180 μm respectively.

The results of this work show that the radial diffusion of the etchant species can affect significantly the silicon etching resolution. The CELT is able to confine the etchant to a very thin layer around the electrode surface, and the etching resolution is thus greatly improved. It can be expected that with a very small tip (from several tenth of micrometer down to several tens of nanometers) and a very thin CEL (around several tens of nanometers), achievement of microstructures with much higher resolution is feasible. In this case, the high resolution etching process needs more precise control of d_{t-s}. It should be noted that it is very difficult to bring a disk electrode precisely to the substrate surface as close as several hundreds or even tens of nanometers. In most cases, the glass-wall surrounding the Pt disk electrode touches the substrate and results in the failure of the d_{t-s} control. Therefore, it