Cu micropatterning on n-Si(1 1 1) by selective electrochemical deposition using an agarose stamp


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Electrochemical wet stamping (E-WETS) was applied for selective deposition of Cu on n-Si(1 1 1) using an agarose stamp. The agarose stamp was first prepared by molding against a master with an array of depressions using its property of plasticity. Cu microstructures were then fabricated directly by preferential electrochemical deposition involving contact between the stamp and a n-Si(1 1 1) workpiece. The gel stamp behaves as a current flow channel between the working electrode and the counter electrode. Furthermore, it simultaneously supplies electrolyte to preferential parts of the n-Si surface. Cu microstructures complementary of those on the master were patterned on the workpiece. The lateral deviation of the fabricated microstructures from those on the master was approximately 0.6%.

1. Introduction

The selective metallization of semiconductor surfaces is of great technological importance. One of the most important applications has been copper wiring in various hierarchies of wiring networks to decrease resistance and tailor RC delay losses [1]. The techniques developed for selective metallization on semiconductor include thermal evaporation, sputtering [2,3] and metal–organic chemical vapor deposition (MOCVD) [4–6]. Complex processes include resist coating, alignment, exposure, development, deposition and resist stripping. As an alternative to deposition from the vapor phase, many metals can be electrodeposited from electrolyte solution onto semiconductors. To fabricate metal micro- or nanostructures on a semiconductor, most approaches generally involve a multi-step procedure, including preparation of a photosensitive resist or growth of a seed layer by electroless plating [7–9]. This type of process has high costs and requires expensive instruments, and hence there is great interest in developing new techniques to metallize semiconductors in a simple and effective way.

Recently, a new approach termed electrochemical wet stamping (E-WETS) was developed by our group [10], for which the principle is illustrated in Fig. 1. The agarose stamp was prepared using its property of plasticity. A hot degassed agarose solution was cast against a Si master with an array of depressions (typical depth, ~50 μm) embossed on its surface. The master was prepared by conventional lithography using inductively coupled plasma (ICP). After cooling, the agarose gel with a negative copy of the microstructures on the master was stripped, and then immersed in electrolyte for some while and finally employed as a patterned stamp (Fig. 1a–c). As shown in Fig. 1d, the electrolyte can be directed and supplied preferentially to the small contact area between the workpiece and the agarose. Selective anodic dissolution or cathodic deposition can take place on the contact area owing to the constant supply of electrolyte from the agarose stamp to the interface. Thus, metal patterns can be formed by selective electrochemical deposition on the contact area between the agarose and the n-Si. Although a patterned agarose stamp is also utilized in the similar reactive wet stamp (r-WETS) method developed by Grzybowski and co-workers [11–14], the electrochemistry method proposed by us provides more controllability and overcomes the limitations of erraticism and non-reproducibility compared with the chemical process of r-WETS. For instance, the Si etch rate in r-WETS by the direct contact of the Si and the agarose stamp is around 2 nm/h, while the anodic Si dissolution rate in E-WETS can be thousands of times faster. Although both methods can be applied to the deposition of metal microstructures, the substrate for the chemical deposition of metal by r-WETS is limited on the agarose [14] and it is very difficult to transfer the deposit to the other useful substrate (e.g. semiconductors).

Here, we applied the E-WETS process to electrochemical deposition, which is opposite to the anodic dissolution of p-Si [10]. Electrochemical deposition onto n-type Si involves electrons in the conduction band and is usually preferred because it is easily
controlled by adjusting the applied potential. In this study, n-type Si was chosen as the working electrode. The aim of the study was to develop an efficient new method for the fabrication of Cu microstructures on Si in order to selectively metallize the silicon surface without any lithography, pattern etching or seeding processes.

2. Experimental

The preparation of micropatterned high-strength agarose (American AMRESCO, biotechnology grade) has been described in detail in our previous paper [10]. The master used here was a Si wafer with microstructures fabricated by ICP. After peeling from the master, micropatterned gels were then soaked in the electroplating solution (normally 0.5 M CuSO4/0.5 M H2SO4) for 2 h. Prior to use, the gels were dried on filter paper for 10 min and then under a stream of N2 for 100 s.

One-sided polished n-Si(1 1 1) samples (phosphorus-doped, 1–20/DEL/cm; N$_D$ =1 015 cm$^{-3}$) were supplied by Huajing Company, China. They were successively degreased in acetone, ethanol and water for 10 min, and then immersed in fresh H2SO4/H2O2 solution (3:1, v/v) for 1 min. Prior to each experiment, samples were etched for 1 min in 5% HF to remove the oxide layer. This treatment creates a hydrophobic silicon surface by forming hydrophobic Si–H bonds, which significantly minimizes lateral spreading of the electrolyte during deposition and hence decreases micromachining deviation. Ohmic contacts were formed by evaporating thin Ti and then Au films consecutively on the back of the wafers.

Electrochemical deposition of copper on n-Si(1 1 1):H was performed using 0.5 M H2SO4/0.5 M CuSO4 prepared with ultrapure water (18.2 MΩ·cm). Electrochemical experiments were performed in a three-electrode glass cell connected to a potentiostat. A saturated calomel electrode (SCE) and a platinum wire served as the reference and counter electrodes, respectively. All potentials are reported versus SCE. The morphology of the deposited copper microstructure was characterized by scanning electron microscopy (LEO 1530).

3. Results and discussion

Electrochemical microfabrication of Cu on n-Si(1 1 1) was performed in a specially designed three-electrode electrochemical cell, as shown in Fig. 1d. To avoid deformation of the stamp under pressure due to the weight of the stamp or interfacial adhesion, the working electrode of Si wafer was placed on top of the patterned stamp in an electrochemical cell filled with a certain concentration of CuSO4. Only the part without the pattern was immersed in the plating electrolyte. The polished side of the Si contacts the agarose stamp, which is far from the solution. This ensures that electrodeposition is limited to the areas of contact between the stamp and the n-Si working electrode.

Fig. 2 shows a typical current–potential curve for n-Si(1 1 1) in a solution of 0.5 M CuSO4/0.5 M H2SO4. The open-circuit potential in this solution was 0.15 V. During the first cycle, Cu deposition initiated at approximately −0.32 V and reached a diffusion-limited current peak at −0.6 V. The reverse scan does not exhibit an anodic peak, which confirms that electrochemical deposition of Cu on n-Si is irreversible. The absence of a stripping peak at anodic potential was due to the large barrier height (~0.6 eV) of the n-Si/Cu junction [15]. According to the growth mechanism of Cu on n-Si, a relatively low deposition potential is required to obtain a Cu film of high quality. Hence, all fabricated Cu microstructures were deposited at −0.4 V in the present study. For deposition of metals onto silicon, experimental conditions should be chosen so that hydrogen evolution is avoided and the surface should be stable during the deposition process. This was achieved by careful selection of the solutions and by avoiding strong hydrogen-evolving conditions.

When a negative potential (~−0.4 V) was applied to the n-Si(1 1 1), the Cu$_{2+}$ was immediately reduced on the n-Si and then it can be supplied continuously to the interface from the bulk of the agarose. The gel stamp plays two important roles: (i) it behaves as a reservoir and supplies Cu$_{2+}$ from the bulk to the silicon–gel inter-
face and (ii) it acts as a current flow channel between the working electrode and the counter electrode. Since electrochemical deposition occurs through three-dimensional progressive nucleation followed by diffusion-limited growth on n-Si [16], the deposition time in the present study was long enough (600–1200 s) for the formation of continuous metal film, as shown in Fig. 3. Various types of copper patterns, including triangular arrays, hexagonal arrays and microgear arrays, were fabricated at a potential of −0.4 V for a deposition time of 600 or 1200 s. Even more complex microstructures, such as herringbone-like ridge arrays and concentric circle arrays (Fig. 3), have been fabricated on n-Si.

Lateral deviation of the fabricated Cu concentric circles was calculated by careful measurement of the size of the master and the fabricated microstructures. As shown in Fig. 4a and b, the inner diameter of the concave concentric ring was measured as 58.8 μm, while that of the copper convex microstructure fabricated by electrochemical deposition was 58.0 μm. The deviation for electrochemical deposition is thus approximately \((58.8 - 58.0)/(2 \times 58.8) \times 100\% = 0.6\%\). Similarly, the distance between two nearest concentric circles was measured as 29.0 μm in Fig. 4a. Correspondingly, the size of the fabricated copper foil was 29.4 μm and the lateral deviation calculated was

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**Fig. 3.** SEM images: (a) curvilinear ridges; (b) hexagonal-shaped Cu array; (c) triangular-shaped Cu array; (d) microgear array; (e) herringbone-like microstructures; and (f) a concentric-rings array. The deposition time was 600 s for (b)–(e) and 1200 s for (a) at a potential of −0.4 V.

**Fig. 4.** (a) Micrograph of a concentric circle on the Si master and (b) Cu concentric circle fabricated on n-Si (1 1 1) with a deposition time of 600 s.
The high precision of Cu patterning and high selectivity of copper deposition resulted from the hydrophobic pretreatment of the Si wafer and hence this treatment can limit the lateral diffusion of the electrolyte across the surface. The thickness of the Cu foils in Fig. 3a and f was measured as approximately 3.23 and 1.75 μm, respectively, by AFM section analysis. Thus, the electrochemical deposition rate can be estimated as ~0.17 μm/min, which is much faster than for r-WETS (0.1–0.3 μm/h) [14]. Furthermore, Cu foil prepared by r-WETS is normally reduced onto the agarose surface with the help of the catalyst and then transferred to a photocurable resin by mechanical detachment. Therefore, it is not easy to use the r-WETS method to transfer Cu foil to other useful substrates.

It should also be noted that the corners of the hexagon (Fig. 3b) and the triangle (Fig. 3c) were not extremely sharp compared to the master microstructures, which might be due to distortion of the gel during the process of being stripped from the mask. However, it is still expected that this technique can be applied to fabricate sub micrometer structures by using a V-shaped master with a smaller contact area.

4. Conclusion

E-WETS can achieve two goals in microfabrication processes. First, it provides a good negative copy of the master microstructures on n-Si at high efficiency because of the fast rate of electrochemical deposition. Second, the process requires no expensive instruments for the pre-experimental procedures and is suitable for fabricating large-scale microstructures at low cost. To increase the thickness of the Cu foil, it is necessary to move the Si workpiece upwards during the deposition process, and a study on this procedure is under way. Using the same mechanism, it is hoped that this new approach can be extended to microstructures of conductive polymers, metal oxides and other materials that are difficult to fabricate using conventional methods.

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