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A novel planarization method based on photoinduced confined chemical etching†

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A photoinduced confined chemical etching system based on TiO$_2$ nanotube arrays is developed for the planarization of the copper surface, which is proved to be a prospective stress-free chemical planarization method for metals and semiconductors.

The planarization of different materials is an essential process to meet the stringent requirements of the subsequent deposition step in the manufacture of integrated circuit devices. Many strategies based on mechanical, physical and chemical methods are used to achieve local and global planarization, such as spin-on deposition, reflow of boron phosphorous silicate glass, spin-etch planarization, reactive ion etching and etch-back.[1] Currently, chemical mechanical planarization (CMP) is commonly recognized as the best method to achieve global planarization.[2] However, CMP has several potential disadvantages including stress cracking, delaminating at weak interfaces, and corrosive attacks from slurry chemicals.[1] To overcome these problems, many researchers have developed new planarization methods including abrasive-free CMP,[3] electrochemical polishing[4] and electrochemical mechanical polishing.[5] Because of the fundamental and technical restrictions of these technologies, such as isotropic removal, limited selectivity of etching and difficulty of process control, the ultra large scale integrated circuit (ULSI) industry needs to develop non-contact, stress-free and gentle planarization/polishing methods, especially when the feature size is decreased to 32 nm and low-*k* dielectric materials replace traditional SiO$_2$ dielectrics.[6]
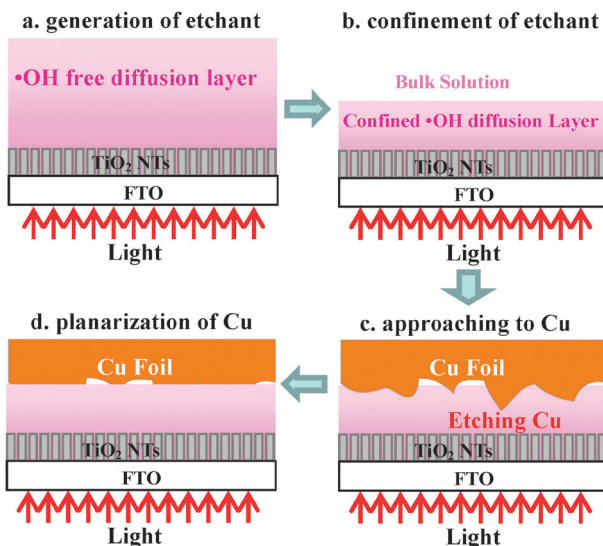
Chemical etching is much gentler than mechanical removal but is difficult to control. Our group has proposed the confined etching layer technique (CELT), in which the precision of chemical etching can be controlled by electrochemical generation of the etchant followed by a scavenging reaction.[7] CELT has been proved to be an effective method to fabricate complex three-dimensional microstructures on different kinds of substrates, including semiconductors such as Si, GaAs[8,9] and metals such as Ni, Cu, Ti, Al and alloys.[10,11] Recently, we developed CELT as a general electrochemical machining method which can be used to perform lathing, planing and polishing.[12] Originating from CELT, for the first time, we present a photoinduced confined chemical etching method for the planarization of Cu surfaces. This method avoids the aforementioned disadvantages of CMP.

It has been reported that •OH generated by the decomposition of H$_2$O$_2$ through the Fenton reaction can act as an etchant to planarize GaN, SiC and Au, lower surface roughness and improve crystalline structure.[13–15] Kim *et al.* revealed that •OH can promote the formation of Cu oxides, and hinder the polishing process.[16,17] Nevertheless, a lack of the end point in CMP means that it is a kind of blind polishing, making it hard to determine when the desired amount of material has been removed or the desired degree of planarization has been obtained. Unlike CMP, in our system, there is no other oxidant (*e.g.*, H$_2$O$_2$) in the reaction solution. In our system, the etchant •OH is generated *in situ* through photocatalytic oxidation by anatase TiO$_2$ nanotube arrays. TiO$_2$ is well known as a useful, non-toxic, environmentally friendly, corrosion-resistant and cheap material. For more discussion on the choosing of the photocatalytic material for use in the current method, see Section S1 of ESI.† When the photocatalyst TiO$_2$ is excited by light, electron–hole pairs are formed and photo-generated holes (h$^+$) oxidize H$_2$O or OH$^-$ to produce •OH.[18] Because •OH is readily consumed in reactions with water or scavenging agents (such as citric acid or glycine),[19,20] the diffusion distance of the etchant •OH is limited and a confined etchant layer (CEL) is formed on the surface of the TiO$_2$ photoelectrode. The surviving etchant •OH will react with the substrate material to smoothen the substrate surface. Cu was selected as a model material to test the feasibility of our planarization method

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† Electronic supplementary information (ESI) available: Experimental details, detection of •OH, SEM and EDS of the pre-treated Cu surface, the effect of glycine on the etching of the Cu surface, SEM images of the Cu surface after etching using spacers of different thickness, the effect of the etching time and a brief comparison of the running cost. See DOI: 10.1039/c3cc42368a

a. generation of etchant

•OH free diffusion layer

TiO₂ NTs
FTO
Light

b. confinement of etchant

Bulk Solution

Confined •OH diffusion Layer

TiO₂ NTs
FTO
Light

d. planarization of Cu

Cu Foil

TiO₂ NTs
FTO
Light

c. approaching to Cu

Cu Foil

Etching Cu

TiO₂ NTs
FTO
Light

Fig. 1 Schematic diagram of the Cu etching and planarization process using the photoinduced confined chemical etching system.

because it is widely used as an interconnect material in ULSIs. The schematic diagram of the photoinduced confined chemical planarization process is presented in Fig. 1. It should be noted here that CELT is a distance-sensitive method, where machining accuracy depends on the thickness of the CEL.[21]
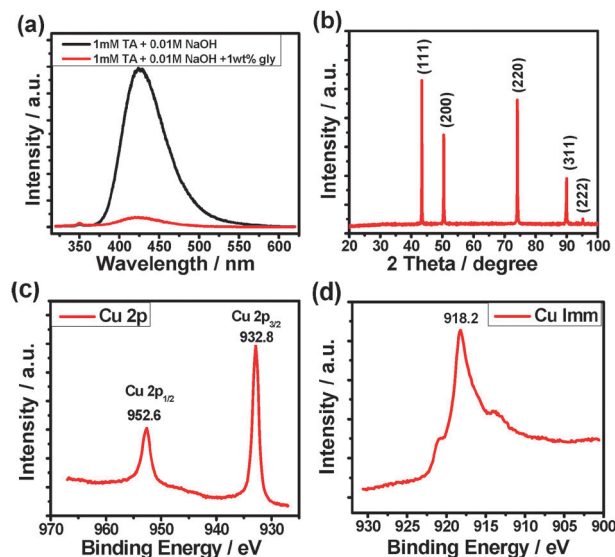
In this communication, we set up a simple experimental device to etch Cu surfaces using this photoinduced confined chemical etching system (see details in Section S1, ESI†). Fig. 2a shows an AFM image of the Cu surface before etching. The entire surface is rough, with a root-mean-square (RMS) and an average roughness (R_a) of 19.0 nm and 14.6 nm, respectively. As shown in Fig. 2b, the photoinduced etching planarized the Cu surface to a certain extent, reducing RMS and R_a to 7.00 nm and 5.32 nm, respectively. This indicates that surface roughness can be reduced by photoinduced confined chemical etching.
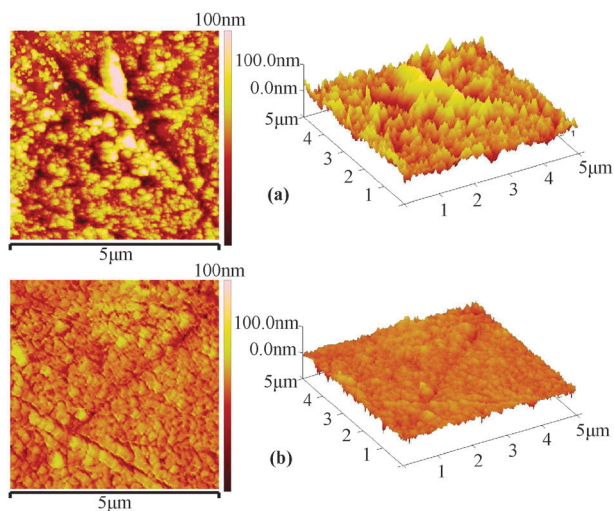
Glycine was chosen as the scavenging agent in our system. The scavenging reaction is actually an hydrogen abstraction from the C–H bonds.[20] In a fluorescent experiment (see details in Section S2, ESI†), the intensity of fluorescence from 2-hydroxy-terephthalic acid decreased dramatically in the presence of glycine (Fig. 3a), indicating that •OH can be scavenged by glycine. Consequently, a CEL of •OH was formed on the surface of the TiO₂ photoelectrode. Glycine can also play the role of a complexing agent to prevent the formation of an oxide layer on the Cu surface. SEM results imply that Cu can be oxidized by •OH and the oxidation product simultaneously reacts with glycine to form a soluble complex, resulting in the ongoing etching (see Fig. S4, ESI†).

To confirm the above deduction, XRD and XPS measurements were carried out. An XRD pattern of the etched Cu surface (Fig. 3b) exhibited five peaks at 2θ of 43.4°, 50.4°, 74.1°, 89.9° and 95.1°. All the diffraction peaks were indexed to metallic Cu. No other peaks were observed in the XRD pattern, indicating that no solid oxide layer was present on the Cu surface after etching. As shown in the XPS results in Fig. 3c, the binding energies of Cu $2p_{3/2}$ and Cu $2p_{1/2}$ obtained from the etched Cu surface appeared to be 932.8 eV and 952.6 eV, respectively. No peak of Cu $2p_{3/2}$ at 933.7 eV for CuO[22] or other typical CuO-satellite peaks for the Cu 2p were observed. These results show that no CuO phase formed on the Cu surface after etching. Since the binding energies of Cu $2p_{3/2}$ for metallic Cu (932.6 eV) and Cu₂O (932.5 eV) were close to each other, the Auger line of Cu lmm was recorded (Fig. 3d). The binding energy of 918.2 eV as well as the α value (Auger parameter + photon energy) of 1851.0 eV were in harmonious accordance with the previously reported values for metallic Cu.[22] All of these results confirmed that no oxide layer formed on the Cu surfaces during the photoinduced confined chemical

Fig. 2 AFM images of (a) pre-treated and (b) etched Cu surfaces (microscope mode: contact). Photoinduced confined chemical planarization was performed in the 1 wt% glycine solution, and the etching time was 4 h.


Fig. 3 (a) Fluorescence spectra obtained for the solution of photoinduced confined chemical etching system containing 1 mM TA and 0.1 M NaOH with and without 1 wt% glycine (excitation at 315 nm); (b) XRD pattern of the etched Cu surface; XPS spectra of (c) Cu 2p region and (d) Cu lmm for the Cu surface after etching in the 1 wt% glycine solution for 4 h.

etching process. Consequently, they reveal that the etching process was continuous. Glycine acted not only as a scavenger but also, more importantly, as a complexing agent to prevent oxidation of the Cu surface in the photoinduced confined chemical etching process. In addition, the concentration of glycine directly affected the thickness of the CEL and has a considerable influence on both etching and planarization.

The distance sensitivity of this method was investigated using PTFE films of different thickness as spacers between the TiO$_2$ photoelectrode and the Cu foil. The Cu surface was pretty rough when the thickness of the PTFE spacer was 35 µm (see Fig. S5a, ESI†), indicating that it was poorly etched. However, when the thickness of the PTFE spacer was increased to 100 µm, etching of the Cu surface slightly occurred and was difficult to recognize on the large-scale SEM image (see Fig. S5b, ESI†). These results clearly reveal the distance sensitivity of our system. If the distance (d) between the photoelectrode and the Cu foil is much smaller than the thickness (δ) of the CEL, the whole surface of the Cu foil will be etched because •OH can attack the whole Cu surface. However, if d is slightly less than δ, only the parts of the Cu surface that are in contact with the CEL will be removed. Once the Cu surface was separated from the CEL, the etching process stopped. It can be concluded that, in our experiment, δ was much larger than 35 µm but matched 100 µm. The effect of etching time was investigated (see Section S6, ESI†). Comparison experiments show that an etching time of 4 h was suitable for our experimental conditions.

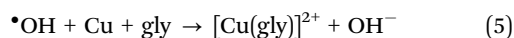In our photoinduced confined chemical planarization system, the following chemical reactions are involved:

(1) Generation reaction of the etchant •OH on the surface of the TiO$_2$ nanotube array based photoelectrode:

$$TiO_2 \xrightarrow{hv} h^+ + e^- \tag{1}$$

$$h^+ + OH^- \rightarrow \bullet OH \tag{2}$$
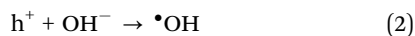
(2) Scavenging reaction to form the CEL:

$$e^- + \bullet OH \rightarrow OH^- \tag{3}$$

$$gly + \bullet OH \rightarrow HOC - COOH + NH_3 + H_2O \tag{4}$$

(3) Etching and planarization of the Cu foil:

$$\bullet OH + Cu + gly \rightarrow [Cu(gly)]^{2+} + OH^- \tag{5}$$

The photoinduced confined chemical etching system involves a photocatalytic process followed by two competitive processes, *i.e.*, scavenging and etching. Although research on the dynamics of the reactions involved in photoelectrochemical kinetics is challenging. The kinetic parameters of these processes are needed to optimize this etching system with regard to efficiency and cost, and are currently being studied.

In summary, a photoinduced confined chemical planarization method for large-area nanofabrication of super smooth surfaces is developed. This method has advantages over CMP, including the absence of contact, free of surface stress and damage, and low cost. The running cost of this method is also discussed in Section S7 of ESI.† Furthermore, because the etchant is generated *in situ* and no strong oxidants are needed in the reaction solution, this method is environmentally friendly, making it attractive for application in the semiconductor industry.

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