CHEMCOMM
Communication
www.rsc.org/chemcomm

Positive and negative photopatterning of metal oxides on silicon *via* bipolar electrochemical deposition†

Hee Cheul Choi and Jillian M. Buriak*

Department of Chemistry, 1393 Brown Laboratories, Purdue University, West Lafayette, IN 47907-1393, USA. E-mail: buriak@purdue.edu

Received (in Cambridge, UK) 24th May 2001, Accepted 13th July 2001
First published as an Advance Article on the web 9th August 2001

Negative and positive microscale patterning of metal oxides is efficiently and rapidly carried out on flat Si(100) surfaces *via* a simple white light assisted bipolar electrochemical process.

The importance of transparent or semi-transparent thin films of high band gap metal oxide semiconductors is rapidly increasing due to a wide range of applications,[1] such as inexpensive photovoltaic cells,[2,3] electrochromic smart windows,[4] ultrafast color displays,[5] and as a base material for room temperature dilute magnetic oxides (DMO).[6] Various techniques such as simple sol–gel preparation followed by dip or spin coating,[7] radio frequency magnetron sputtering,[8] chemical vapor deposition,[9] or laser ablation[10] have been used for many years to prepare metal oxide thin films. Electrochemical deposition has, however, been the focus of much recent interest due its comparable simplicity of required apparatus, and the possibility for either kinetic or thermodynamic control of products *via* galvanostatic or potentiostatic modes.[11] Since Switzer introduced an electrosynthetic technique for preparation of metal oxides in 1987,[12] there have been many reports outlining electrochemical deposition of different metal oxides on various types of conducting substrates.[11] Generally, metal oxide deposition can be accomplished by either anodic or cathodic bias, depending on the desired oxide.[11,13–17] Patterning of metal oxide thin films is central to their application in technological devices to allow for spatial definition.[18] Here we describe a general white light promoted electrochemical metal oxide photopatterning procedure on n- or p-type Si(100) that allows, in a very straightforward and efficient manner, both negative and positive masking, as shown in Fig. 1.

A number of electrochemical deposition parameters were systematically varied to determine the requirements for positive and negative pattern formation on Si(100) substrates, as summarized in Table 1. In addition, the influence of different procedures on the metal oxide structures was determined by X-ray diffraction (XRD) and scanning electron microscopy (SEM). The first four processes, 1P–4P, are illuminated through a grid mask with white light, and the second four, processes 1–4, do not involve photopatterning and are used as reference samples. Only processes 3P and 4P lead to positive and negative photopatterning, depending upon the doping of the silicon. Processes 1P and 2P, on the other hand, lead to homogeneous deposition of metal oxides across the entire face of the exposed silicon surface. Fig. 2 shows the results of positive and negative photopatterning experiments formed *via* process 3P with zinc nitrate on n-type (left) and p-type (right) silicon substrates as visualized by optical microscopy (similar patterns of CeO_2 and Cr_2O_3 are shown in the ESI†). The dark areas in Fig. 2 are underivatized Si, and the light areas the metal oxide, as determined by XRD (*vide infra*). The metal oxides deposit in the shaded region when the substrate is n-type Si, and exclusively in the illuminated area on p-type Si. Process 4P, involving *in situ* heating and elimination of the secondary sintering step, yields similar results and indicates that metal oxides can be successfully patterned regardless of the heating process. Earlier work has shown that in the case of metal oxides

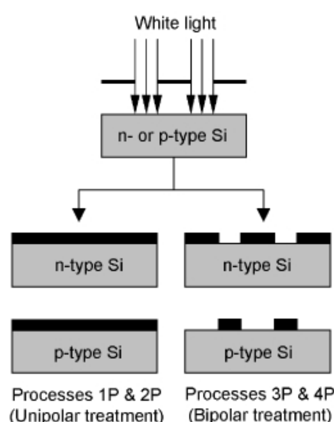

Fig. 1 Schematic view of electrochemical patterning of ZnO on Si(100) substrates with white light illumination through a photomask. Positive and negative patterning can be achieved through bipolar electrochemical treatment.

Table 1 Outline of the 8 different metal oxide deposition approaches for synthesis of ZnO, CeO_2 and Cr_2O_3 on Si(100). Processes 1–4 do not involve patterning, while processes 1P–4P differ only in that they are patterned *via* simultaneous white light illumination with a photomask

Photopatterning of metal oxides on Si	
Method	Treatment
Process 1P	Unipolar (cathodic) → *ex situ* sintering at 350 °C
Process 2P	Unipolar (cathodic) → *in situ* heating at 60 °C
Process 3P	Bipolar (anodic followed by cathodic) → *ex situ* sintering at 350 °C
Process 4P	Bipolar (anodic followed by cathodic) → *in situ* heating at 60 °C
Non-photopatterned deposition of metal oxides on Si	
Process 1	Unipolar (cathodic) → *ex situ* sintering at 350 °C
Process 2	Unipolar (cathodic) → *in situ* heating at 60 °C
Process 3	Bipolar (anodic followed by cathodic) → *ex situ* sintering at 350 °C
Process 4	Bipolar (anodic followed by cathodic) → *in situ* heating at 60 °C

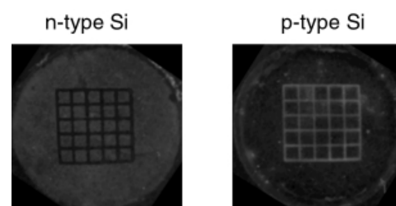

Fig. 2 Optical micrographs of the patterned ZnO films on n- and p-type Si. The diameter of the circular area is 1.0 cm. The light areas correspond to the metal oxide deposits while the dark areas correspond to underivatized Si surfaces.

† Electronic supplementary information (ESI) available: experimental details, XRD profiles, optical and SEM micrographs. See http://www.rsc.org/suppdata/cc/b1/b104586p/

DOI: 10.1039/b104586p

This journal is © The Royal Society of Chemistry 2001

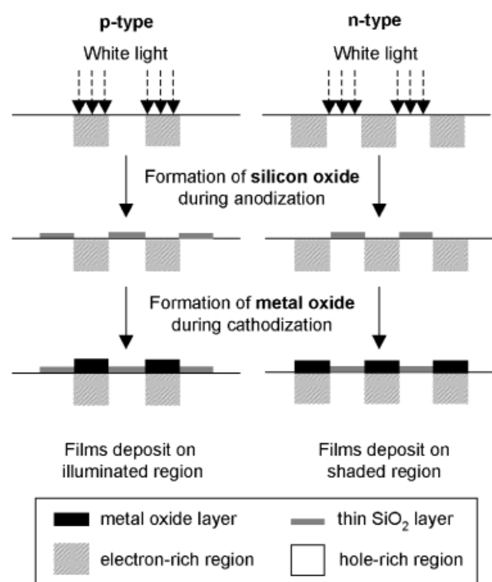

Fig. 3 Schematic illustration of the effect of light illumination, allowing selective photopatterning of various metal oxides on n- and p-type silicon, outlining the importance of doping type. Illumination coupled with application of an anodic bias induces holes to localize in the illuminated areas for n-type Si, and in the shaded areas for p-type Si. Therefore, silicon oxide formation occurs in positive and negative areas, relative to the photomask. The insulating characteristics of the SiO_2 layer prevent metal oxide deposition during the subsequent cathodic step.

which can be formed *via* anodic oxidation on silicon (Tl_2O_3 for example), photopatterning occurs only in the illluminated area of n-type silicon.[14] The bipolar electrochemical deposition approach therefore demonstrates excellent and unique selectivity for both negative and positive photopatterning of different metal oxides on silicon substrates.

While unipolar cathodic metal oxide deposition with either *ex situ* sintering[19] or *in situ* heating[15] is known in the literature, bipolar deposition, on the other hand, is not. Processes 1–4 were examined to prepare large areas of metal oxide for characterization, and to ensure that the same material is produced under photopatterning conditions (processes 1P–4P). XRD experiments reveal that the ZnO film deposited by cathodic unipolar treatment (processes 1 and 2), with or without illumination, is of a wurtzite crystal structure (JCPDS table 35–1451).[20] The XRD patterns of ZnO deposited through processes 3 and 4 on n-type Si are identical to processes 1 and 2, also of a wurtzite structure, and little difference in the crystal structure between *in situ* (process 3) and *ex situ* heating (process 4) is noted. The XRD spectra of the photopatterned metal oxides indicate that the crystal structures formed under these conditions (processes 3P and 4P) are the same as processes 1–4, and thus the photopatterning process does not have a major influence on the nature of the metal oxide. The details of XRD studies of all the metal oxides studied here are included in the ESI†. SEM studies revealed that a porous granular thin film is formed *via* all of these electrodeposition procedures ESI†. The mechanism for cathodic metal oxide formation is most likely nitrate reduction, forming OH^- which precipitates the metal hydroxide/oxide.[15]

The bipolar electrochemical deposition technique that leads to patterning requires application of a short period of anodic current to the silicon surface (+ 5 mA cm^{-2}) for 5 s, prior to cathodization (−5 mA cm^{-2}) for 5 min. As a control experiment, the silicon surface (both n- and p-type) was illuminated through a photomask during application of a cathodic current for 5 min, without the preceding short anodic pulse. Under these conditions, only homogeneous deposition of metal oxides occurs over the entire substrate surface; no patterning is observed, confirming the importance of the short anodic pretreatment for patterning ZnO, CeO_2 and Cr_2O_3. Another control experiment involved cathodic treatment after light illumination on n- or p-type Si in the deposition solution for 10–60 s without any applied current. Again, only a homogeneous thin film was achieved, as observed under cathodic unipolar treatment. These results clearly show that the deposition of metal oxides and their patterning is not controlled by the generation of excess holes during the electrochemical metal oxide deposition process.

On the n-type Si electrode, hole migration under positive bias to the illuminated area takes place, leading to patterned silicon oxide formation which requires holes at the surface; the holes are provided by electron tunneling from the valence band to the conduction band. Therefore, the applied current will flow preferentially through the illuminated areas, giving rise to selective silicon oxide growth in these regions. The silicon oxide formed is expected to act as an electronic barrier. Thus, upon application of cathodic current, metal oxide deposition will take place only in the dark areas because the SiO_2 layer blocks current in the illuminated regions, as shown schematically in Fig. 3. On the p-type Si electrode, on the other hand, holes are the majority charge carriers and thus charge separation upon the illumination is not expected at a low bias of +5 mA cm^{-2}, *i.e.* the whole area should be oxidized. In this case, however, the onset of the photocurrent may be at a more positive potential than the breakdown potential of the bulk silicon band gap (electron tunneling from the valence band to the conduction band at the surface), leading to metal oxide deposition only in the illuminated areas. Further investigation is presently being performed in order to elucidate these mechanisms more clearly.

We gratefully acknowledge support from NSF, the Purdue Research Foundation (fellowship to H. C. C.) and Purdue University. J. M. B. is holder of a Sloan Research Fellowship (2002–2002) and is a Cottrell Teacher-Scholar of Research Corporation (2000–2002).

Notes and references

1 C. Feldmann and H.-O. Jungk, *Angew. Chem., Int. Ed.*, 2001, **40**, 359.
2 T. Yoshida and H. Minoura, *Adv. Mater.*, 2000, **12**, 1219.
3 T. Yoshida, K. Terada, D. Schlettwein, T. Oekermann, T. Sugiura and H. Minoura, *Adv. Mater.*, 2000, **12**, 1214.
4 C. G. Granqvist, *Handbook of Inorganic Electrochromic Materials*, Elesevier, Amsterdam, 1995.
5 M. Grätzel, *Nature*, 2001, **409**, 575; F. Campus, P. Bonhôte, M. Grätzel, S. Heinen and L. Walder, *Sol. Energy Mater. Sol. Cells*, 1999, **56**, 281.
6 Y. Matsumoto, M. Murakami, T. Shono, T. Hasegawa, T. Fukumura, M. Kawasaki, P. Ahmet, T. Chikyow, S.-Y. Koshihara and H. Koinuma, *Science*, 2001, **291**, 854.
7 N. Özer, D.-G. Chen and T. Büyüklimanli, *Sol. Energy Mater. Sol. Cells*, 1998, **52**, 223.
8 O. Takai, M. Futsuhara, G. Shimizu, C. P. Lungu and J. Notue, *Thin Solid Films*, 1998, **318**, 117.
9 J. Hu and R. G. Gordon, *J. Appl. Phys.*, 1992, **71**, 880.
10 S. V. Prasad, S. D. Walck and J. S. Zabinski, *Thin Solid Films*, 2000, **360**, 107.
11 G. H. A. Therese and P. V. Kamath, *Chem. Mater.*, 2000, **12**, 1195.
12 J. A. Switzer, *Am. Ceram. Soc. Bull*, 1987, **66**, 1521.
13 R. Chaim, S. Almaleh-Rockman and L. Gal-Or, *J. Am. Ceram. Soc.*, 1994, **77**, 3202.
14 R. J. Phillips, M. J. Shane and J. A. Switzer, *J. Mater. Res.*, 1989, **4**, 923; J. A. Switzer, *J. Electrochem. Soc.*, 1986, **133**, 722.
15 M. Izaki and T. Omi, *J. Electrochem. Soc.*, 1996, **143**, L53; M. Izaki, *J. Electrochem. Soc.*, 1999, **146**, 4517.
16 K. J. Stevenson, G. J. Hurtt and J. T. Hupp, *Electrochem. Solid State*, 1999, **2**, 175.
17 C. Natarajan and G. Nogami, *J. Electrochem. Soc.*, 1996, **143**, 1547; E. A. Meulenkamp, *J. Electrochem. Soc.*, 1997, **144**, 1664.
18 D. Gal, G. Hodes, D. Lincot and H.-W. Schock, *Thin Sold Films*, 2000, **361**–**362**, 79.
19 V. Srinivasan and J. W. Weidner, *J. Electrochem. Soc.*, 1997, **144**, L210.
20 *Joint Committee on Powder Diffraction Standards*, Set 36, No 1451, International Center for Diffraction Data, Swarthmore, PA, 1986.