

# Effect of gold coating on local oxidation using an atomic force microscope

J. S. Hwang,<sup>a)</sup> Z. Y. You, S. Y. Lin, and Z. S. Hu

*Institute of Optoelectronic Sciences, National Taiwan Ocean University, Keelung, Taiwan*

C. T. Wu and C. W. Chen

*Department of Material Science and Engineering, National Taiwan University, Taipei, Taiwan*

K. H. Chen

*Institute of Atomic and Molecular Sciences, Academia Sinica, Taipei, Taiwan*

(Received 20 December 2004; accepted 9 March 2005; published online 11 April 2005)

A simple method to enhance atomic force microscopy local oxidation by coating the substrate with a thin layer of gold is reported. The effect of gold coating is demonstrated experimentally by atomic force microscopy oxidation at various thicknesses of gold on Si and InP. Oxide heights reaching 30 nm are easily achieved on silicon at rates 10 times greater than traditional methods. The gold layer is assumed to increase conductance and current during oxidation, thereby reducing decline in growth rates caused by the increasing resistance of the growing oxide layer itself. Improvement in growth rate and height increases with increasing gold thickness up to a maximum height, but beyond that thickness the heights and rates decrease because the gold layer itself becomes a barrier to the migration of oxyions. The presented method is demonstrated to improve the oxidation rate and height on normal and highly resistive substrates, with lower requirements for applied voltage during oxidation. © 2005 American Institute of Physics. [DOI: 10.1063/1.1901804]

Local oxidation using an atomic force microscope (AFM), or AFM nano-oxidation, is a promising scanning-probe-based lithography method suitable for fabrication of nanometer scale structures and devices.<sup>1–8</sup> The tremendous electric field built by the applied voltage and the automatically formed “water bridge” (water meniscus) between the AFM conducting tip and the substrate in an ambient environment are capable of inducing anodic oxidation on the substrate and forming nanoscale oxide patterns. The electric field, reaching the order of  $10^9$  V/m, has been applied to the local oxidation of silicon, GaAs,<sup>9</sup> silicon nitride,<sup>5,10</sup> silicon carbide,<sup>11</sup> metals,<sup>12–15</sup> and even oxides,<sup>7,16–18</sup> including high-temperature superconductors. Fabrication of nanoelectronic devices such as transistors,<sup>1,7,19–21</sup> single electron memory,<sup>4</sup> Josephson junctions, and superconducting quantum interference devices<sup>6,18</sup> (SQUID) with AFM nano-oxidation has been demonstrated.

For potential mass production of nanodevices, it is essential to develop nano-oxidation techniques with high growth rates, which will enable not only increased final oxide heights but also easy oxidation of other than highly doped substrates. Tello *et al.*<sup>22</sup> have reported on this issue by replacing the water bridge with alcohol, thereby attaining oxide heights exceeding 20 nm on silicon with a growth rate 4–5 times higher than those obtained under the same conditions in water. Simpler than Tello’s alcohol bridge, our present study continues the use of the traditional water bridge in an ambient environment. The proposed method can produce oxides reaching a few tens of nanometers in height with an estimated growth rate 10 times greater than traditional water-based methods under identical conditions on semiconductor substrates including Si and InP at low applied voltage, without requiring a highly doped substrate. The nano-oxidation of semi-insulating InP is reported, in contrast

to the tip-induced oxidation observed during carrier profiling using scanning spreading resistance microscopy<sup>23</sup> on normally doped InP substrates.

Our method requires a simple coating of the substrate with gold, which can presumably be replaced with other noble metals. Figure 1 shows the schematic diagram of the method. It is known that during the process of conventional AFM oxidation with constant applied voltage, as the insulating oxide is forming, the total resistance of the circuit increases rapidly with simultaneous decrease of the current flow. The current flow helps drive oxyanions<sup>2,24</sup> such as  $\text{OH}^-$  and  $\text{O}^{2-}$  in the water bridge through the forming oxide barrier to the  $\text{SiO}_2/\text{Si}$  interface, inducing further oxidation, but both current reduction and the diffusion barrier of the formed oxide limit growth rate and the final growth height of the silicon oxide. Therefore, coating the substrate with a thin conductive layer such as gold reduces the current decay that results from increasing oxide resistance. Likewise, the increased surface conductivity from the coating also helps enlarge initial current flow. However, it should be noted that the conductive layer itself can become a diffusion barrier at larger thicknesses, which implies the existence of an optimal

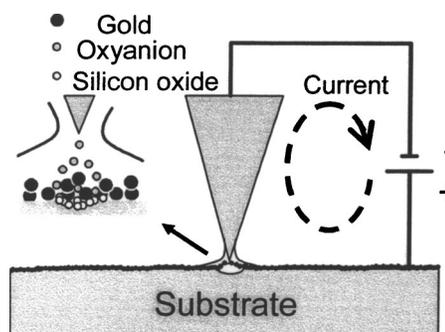


FIG. 1. Schematic diagram of gold coating enhanced AFM local oxidation.

<sup>a)</sup> Author to whom correspondence should be addressed; electronic mail: hjsspin@mail.ntou.edu.tw

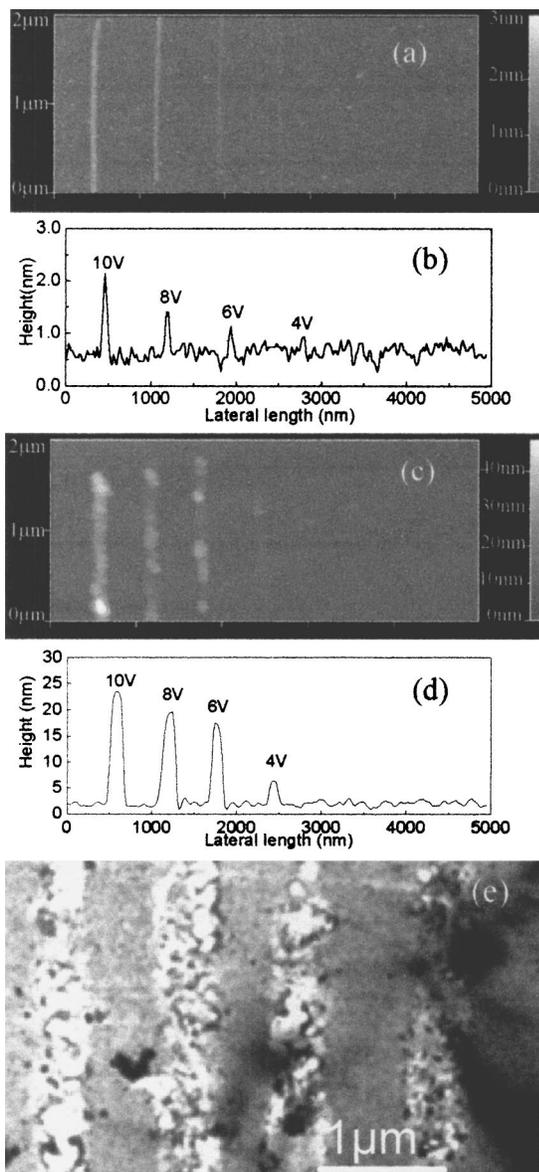


FIG. 2. (a)–(d) Typical AFM images and oxide height of local oxidation on (a), (b) pure silicon substrate and (c), (d) silicon substrate with a 29-nm gold coating, at different applied voltages. (e) TEM planar view micrograph of oxide lines (brighter part) grown by AFM oxidation on silicon substrate with a 22-nm gold coating at an applied voltage of 10 V.

conductive layer thickness for enhancement of local oxidation.

We have demonstrated the effect on nano-oxidation of gold coating using a NTMDT P47H AFM. Surface-cleaned *p*-type (100) silicon (with a resistivity of 4.1 Ω cm) and semi-insulating InP (100) (AXT, Inc., with a resistivity of  $5.5 \times 10^6$  Ω cm and a carrier concentration of  $1.1 \times 10^{13}$  cm<sup>-3</sup>, evaluated under a standard Hall effect measurement system) were coated with gold layers of various thicknesses using a sputter coater (Emitech K575X) before local oxidation. Local oxidation was performed using the tapping mode by applying a negative pulse voltage of 84 ms within 1 Hz duration on a conductive Pt-coated silicon tip scanning at the speed of 3000 Å/s under a humidity of 70%. A JEOL JEM-2000FX transmission electron microscope (TEM) was used to observe the grown oxide.

Figures 2(a)–2(d) show typical AFM images and oxide heights of oxidation performed on a pure silicon substrate

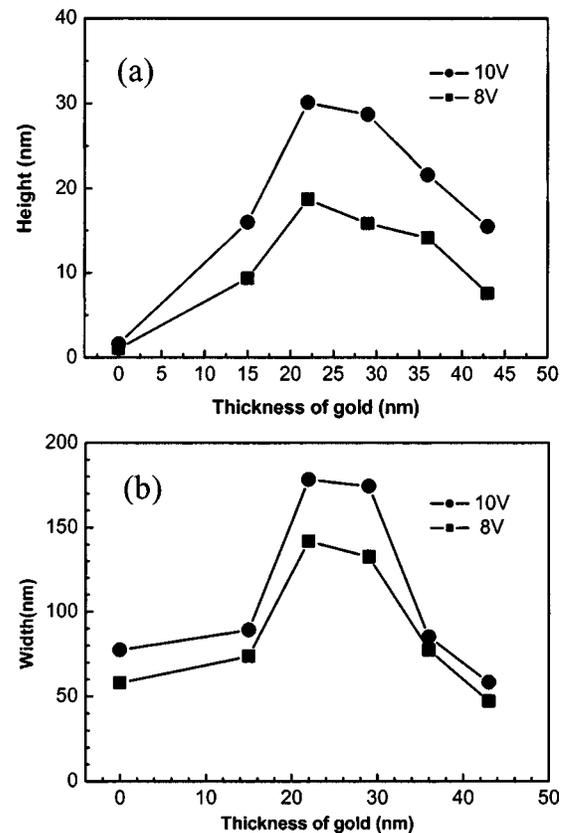


FIG. 3. AFM oxidative (a) height and (b) width dependence on gold thickness under two applied voltages (8 and 10 V); the solid lines connecting data points are only for visual guides.

[Figs. 2(a) and 2(b)] and a Au-coated silicon substrate [Figs. 2(c) and 2(d)] at various applied voltages. Our results show the oxide height on Au-coated silicon is much greater than that grown on a pure silicon substrate, but with irregular height along the oxidative lines. After examination by AFM, the irregular height seems due to peeled portions [an unusually bright spot in Fig. 2(c)] of the gold film extruded by oxide grown beneath the metal film. This interpretation was reinforced by the existence of a trench on the substrate after the oxide line was etched away in HF and by a TEM planar view micrograph shown in Fig. 2(e), which further evidenced the oxide grown beneath the gold layer. Note that the oxide lines in the TEM micrograph, whose width ( $\sim 500$  nm) is apparently larger than that in Fig. 2(d), was intentionally grown at high humidity ( $\sim 90\%$ ) to make possible the TEM sample preparation under the optical microscope. The dependence of oxide height on applied voltage for the AFM images of Figs. 2(a) and 2(c) can be seen respectively in Figs. 2(b) and 2(d), both of which demonstrate the typical decay in height at lower voltages. Nevertheless, the voltage required to attain the same oxide height for the gold-coated sample is apparently much lower than that needed for pure silicon. Since oxidation of the two samples was performed under identical conditions and identical oxidation times, a comparison of Figs. 2(b) and 2(d) shows an estimated growth rate on the Au-coated silicon substrate that is at least 10 times greater than without Au coating.

For further clarification of the effect of gold coating, local oxidation on silicon substrates coated with different thicknesses of the gold layer were conducted. The relations of the average height and width of the oxide lines to the

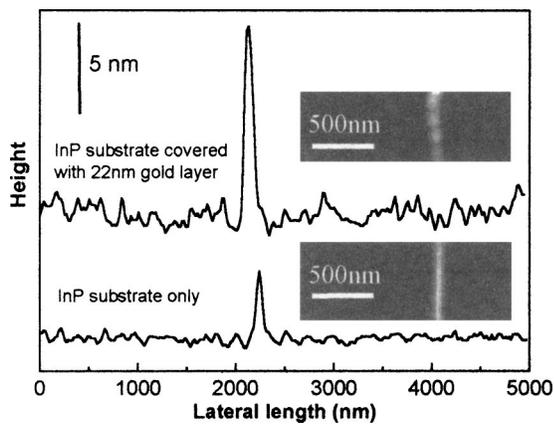


FIG. 4. AFM oxide heights of local oxidation on (a) InP and (b) InP with a 22-nm gold coating; insets show the corresponding AFM images.

thickness of the gold layer are shown, respectively, in Figs. 3(a) and 3(b). Figure 3(a) shows that as the thickness of gold increases, the height and width of the oxide also increase, reaching a maximum at 22 nm of gold. As the thickness of the gold layer increased further, the vertical and lateral dimensions of the grown oxide decreased. This behavior can be explained by the concepts discussed earlier in this letter (Fig. 1), i.e., the thin gold layer during oxidation increases both conductance and current, which helps migration of oxyions to the silicon/SiO<sub>2</sub> interface. However, when the gold layer becomes thicker than a certain value, it becomes a diffusion barrier and hampers migration of oxyions through the gold to the Si/SiO<sub>2</sub> interface. With regard to this, it is believed that microcracks or slits between gold grains in the sputtered gold layer constitute the main channels for oxyion migration. It should be mentioned that oxide growth stopped at a gold thickness beyond about 80 nm, which precludes the possibility of impurities in gold forming the oxide.

The effect of gold coating on oxidation was examined also on semi-insulating InP (100) substrates, with behavior similar to that found for silicon. Figure 4 compares the oxidation results of InP with and without gold coating, with AFM images shown in the insets. The height of the oxide lines with gold was about three times higher than without gold. We report here the AFM local oxidation on semi-insulating InP. Of note is the surprising ease of AFM oxidation on the pure semi-insulating InP substrate with a  $5.5 \times 10^6 \Omega \text{ cm}$  resistivity. Compared to the difficulty of local oxidation of other high-resistivity substrates, the phenomenon indicates a negative change of Gibb's free energy during the reaction of the system at high applied voltage, showing the importance of chemical thermodynamics in the technique of AFM oxidation.

In conclusion, a simple method to enhance the AFM local oxidation by coating the substrate with a thin layer of gold has been reported. We have demonstrated the effect of

gold coating on the AFM local oxidation of various substrates including Si and InP. The grown oxidative heights can be increased to a few tens of nanometers with deposition of an appropriate thickness of gold on the surface of the silicon substrate for increased conductance and current. When the thickness of the gold is increased beyond a certain level, the grown oxidative height then decreases due to limited migration of oxyions through the gold layer. The presented method, which assists oxidation on resistive substrates by improving efficiency as well as lowering the voltage required for oxidation, improves chances to realize AFM-based mass production of nanodevices.

The authors are grateful for financial support from the National Science Council (Grant No. NSC93-2112-M-001), Taiwan.

- <sup>1</sup>E. S. Snow, P. M. Campbell, F. A. Buot, D. Park, C. R. K. Marrian, and R. Magno, *Appl. Phys. Lett.* **72**, 3071 (1998).
- <sup>2</sup>R. Garcia, M. Calleja, and H. Rohrer, *J. Appl. Phys.* **86**, 1898 (1999).
- <sup>3</sup>E. B. Cooper, S. R. Manalis, H. Fang, H. Dai, K. Matsumoto, S. C. Minne, T. Hunt, and C. F. Quate, *Appl. Phys. Lett.* **75**, 3566 (1999).
- <sup>4</sup>K. Matsumoto, Y. Gotoh, T. Maeda, J. A. Dagata, and J. S. Harris, *Appl. Phys. Lett.* **76**, 239 (2000).
- <sup>5</sup>F. S. Chien, Y.-C. Chou, T. T. Chen, W.-F. Hsieh, T. S. Chao, and S. Gwo, *J. Appl. Phys.* **89**, 2465 (2001).
- <sup>6</sup>V. Bouchiat, M. Faucher, C. Thirion, W. Wernsdorfer, T. Fournier, and B. Pannetier, *Appl. Phys. Lett.* **79**, 123 (2001).
- <sup>7</sup>L. Pellegrino, I. Pallecchi, D. Marré, E. Bellingeri, and A. S. Siri, *Appl. Phys. Lett.* **81**, 3849 (2002).
- <sup>8</sup>A. Dorn, M. Sigrist, A. Fuhrer, T. Ihn, T. Heinzel, K. Ensslin, W. Wegscheider, and M. Bichler, *Appl. Phys. Lett.* **80**, 252 (2002).
- <sup>9</sup>Y. Okada, Y. Iuchi, M. Kawabe, and J. S. Harris, Jr., *Appl. Phys. Lett.* **88**, 1136 (2000).
- <sup>10</sup>F. S. S. Chien, J. W. Chang, S. W. Lin, Y. C. Chou, T. T. Chen, S. Gwo, T. S. Chao, and W. F. Hsieh, *Appl. Phys. Lett.* **76**, 360 (2000).
- <sup>11</sup>X. N. Xie, H. J. Chung, C. H. Sow, and A. T. S. Wee, *Appl. Phys. Lett.* **84**, 4914 (2004).
- <sup>12</sup>M. S. Hagedorn, D. D. Litfin, G. M. Price, A. E. Gordon, and T. K. Higman, *J. Vac. Sci. Technol. B* **14**, 4153 (1996).
- <sup>13</sup>E. S. Snow and P. M. Campbell, *Science* **250**, 1639 (1995).
- <sup>14</sup>H. Sugimura, T. Uchida, N. Kitamura, and H. Masuhara, *Appl. Phys. Lett.* **63**, 1288 (1993).
- <sup>15</sup>K. Matsumoto, M. Ishii, K. Segawa, Y. Oka, B. J. Vartanian, and J. S. Harris, *Appl. Phys. Lett.* **68**, 34 (1996).
- <sup>16</sup>Y. R. Ma, C. Yu, Y. D. Yao, Y. Liou, and S. F. Lee, *Phys. Rev. B* **64**, 195324 (2001).
- <sup>17</sup>R. W. Li, T. Kanki, H. A. Tohyama, J. Zhang, H. Tanaka, A. Takagi, T. Matsumoto, and T. Kawai, *J. Appl. Phys.* **95**, 7091 (2004).
- <sup>18</sup>I. Song, B. M. Kim, and G. Park, *Appl. Phys. Lett.* **76**, 601 (2000).
- <sup>19</sup>P. M. Campbell, E. S. Snow, and P. J. McMarr, *Appl. Phys. Lett.* **66**, 1388 (1995).
- <sup>20</sup>E. S. Snow, P. M. Campbell, R. W. Rendell, F. A. Buot, D. Park, C. R. K. Marrian, and R. Magno, *Appl. Phys. Lett.* **72**, 3071 (1998).
- <sup>21</sup>I. Pallecchi, L. Pellegrino, E. Bellingeri, A. S. Siri, and D. Marre, *J. Appl. Phys.* **95**, 8079 (2004).
- <sup>22</sup>M. Tello and R. Garcia, *Appl. Phys. Lett.* **83**, 2339 (2003).
- <sup>23</sup>M. W. Xu, P. Eyben, T. Hantschel, and W. Vandervorst, *Jpn. J. Appl. Phys., Part 1* **41**, 1048 (2002).
- <sup>24</sup>A. E. Gordon, R. T. Fayfield, D. D. Litfin, and T. K. Higman, *J. Vac. Sci. Technol. B* **13**, 2805 (1995).