Stable field emission of ion-sputtering-induced Si nanocone arrays

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Received May 15, 2013; accepted September 16, 2013; posted online November 4, 2013

Silicon nanocone arrays with metal silicide (Fe and Cr)-enriched apexes are fabricated on Si (100) substrate by the Ar^+ ion bombardment method. The nanocone arrays show excellent field emission properties. A high current density (J) of ∼0.33 mA/cm^2 under a field of ∼3 V/μm, a very low turn-on field of ∼1.4 V/μm, and a very large enhancement factor of ∼9466 are also obtained. The emission J of Si nanocone arrays remains extremely stable for long periods of time (24 h).

OCIS codes: 160.2100, 160.4236.

doi: 10.3788/COL201311.111601.

Field emission has attracted significant attention over the last few decades because of the important role it plays in devices such as X-ray tubes[1−3], electron microscopes, and flat panel displays[4]. Carbon nanotubes[5,6] have been demonstrated to be ideal field emission materials because of their high aspect ratio, excellent conductivity, and good chemical and thermal stability[7,8]. Silicon field emission cathodes[9−13] also present unique advantages. For example, the cathodes can be easily integrated with a field emission driving circuit and focused into sharp micro points to achieve higher current densities at lower fields. Thus, published research work based on the investigation of field emission properties of Si emitters is widely available.

Chang *et al.*[14] reported that the turn-on fields of Au- and Pt-coated Si arrays are 2.9 and 3.65 V/μm, respectively. Zhao *et al.*[15] reported that the turn-on field of Au film-coated silicon nanowires (1.95 V/μm) is lower after annealing because Au-Si nanoparticle decoration enhances electron transport and reduces the surface potential barrier height of the silicon nanowires. Yang *et al.*[16] found that the enhancement factor of polycrystalline diamond-coated silicon emitters is 8330. Besides the materials mentioned above, other materials may be formed into silicon points to enhance the field emission properties of silicon. These materials include carbon[17] and $CoSi_2$/TaN[18], among others. The added materials reduce the work function (ϕ) so that the field emission properties of the Si emitters can be enhanced. However, for practical applications, the performance of field emission devices developed to date must be further improved, especially in terms of their long-term stability.

To the best of our knowledge, induction of field emission from Si nanocone arrays with Fe and Cr metal silicides at their apexes by Ar^+ ion bombardment, a technique that combines metal silicide coatings with nanocone formation, has yet to be reported. The field emission properties of Si nanocone arrays with metal silicide (Fe and Cr)-enriched apexes are investigated in this letter. The nanocone arrays show excellent field emission properties, and the emission current density (J) remains ultra-stable for long periods of time.

Si field emitter nanocone arrays, the optical properties of which are described in detail elsewhere[19,20], were fabricated on Si (100) by Ar^+ ion bombardment at 800 °C for different time durations. The Si (100) wafers (p-type; doping level, 2×10^{15} cm^{-3}; thickness, 1 mm) were degreased in a solution of H_2SO_4:H_2O_2=1:1 for 30 min, rinsed with deionized water for 5 min, and supersonically cleaned in acetone and alcohol for 15 min. The clean Si sample was then transferred into a high-vacuum chamber equipped with a Kaufmann-type ion source for ion bombardment. The Kaufmann source (Ar^+ ion source; ion energy, 1.5 keV; J, 1000 μA/cm^2) normally faced the polished side of the Si sample at a distance of 18 cm. Irradiation was carried out for 25, 35, and 45 min. The Si sample was fixed by a stainless steel mask consisting of Fe and Cr with a hole of 8 mm in diameter. Because the ion beam size (5 cm) was much larger than the mask hole, both the mask and the Si sample were irradiated simultaneously.

The Si substrate was fixed to a polished aluminum plate for field emission property measurements. The cone arrays were used as cathodes at a distance of 100 μm from the anode, which was composed of indium-tin-oxide (ITO) glass, to form a diode structure. The area of the emitters was ∼0.5 cm^2. The field emission properties of the Si nanocone arrays were measured in a vacuum chamber under a pressure of ∼2×10^{-5} Pa. Direct current (DC) voltage was swept from 0 to 550 V with an interval of 50 V to measure the corresponding field emission currents (ammeter range, 0 to 2×10^4 μA; sensitivity, 50 Ω/V) at 1-min intervals.

Scanning electron microscope (SEM) images of the ultimate nanocone arrays are shown in Fig. 1. The nanocone arrays do not completely separate from each other after bombardment for 25 min. When the time duration increases to 35 min, thoroughly separated nanocone arrays are formed, but they are short and have a small curvature. As the bombardment time is further increased to 45 min, the nanocones become longer and show a larger curvature. Each cone has the same crystallographic ori-

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entation on the substrate. Figure 2 shows the X-ray diffraction (XRD) spectra of a Si nanocone array (measurement spot, surface of the Si substrate; spot diameter, ~1 mm). Zhou *et al.*[19] proved that metallic Fe and Cr only exist at the apex of a nanocone array and showed that the rest of the array is metal-free. The atomic percentages of Fe and Cr at the apex are 19.6% and 4.5%, respectively. As only a small amount of Cr exists at the apex of the array, the Cr content may be expected to be very low in the entire Si substrate. Few FeSi peaks may be observed (Fig. 2). The formation of silicides is extensively explained by Qiu *et al.*[20].

According to Fowler *et al.*[21], the J versus applied electrical field (E) curve is given by

$$J = A\frac{\beta^2 E^2}{\Phi}\exp\Big(-\frac{B\Phi^{3/2}}{\beta E}\Big), \qquad (1)$$

where $A = 1.54 \times 10^{-6}$ AeV/V^2, $B = 6.83 \times 10^3$ (V/μm) eV$^{-3/2}$, β is the field enhancement factor, Φ is the work function (eV), and E (V/μm) is the applied electric field, which is the nominal field and not the local field at the apexes. Equation (1) can be simplified to a linear form from which Fowler-Nordheim (FN) plots can be drawn. Figures 3(a) and (b) show the J versus E curves of Si nanocone arrays bombarded for different times as well as their corresponding FN plots. The turn-on field, which is defined as the E corresponding to a J of ~10 μA/cm^2, was estimated from the $J - E$ curve.

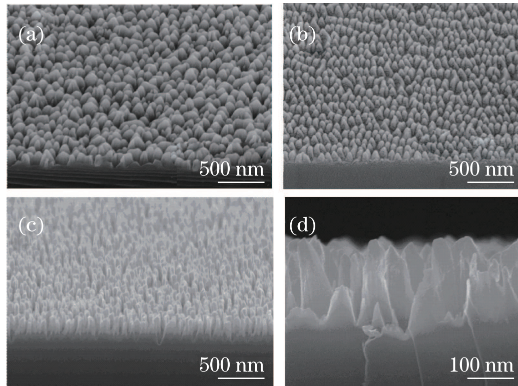

Fig. 1. SEM images of the Si nanocone arrays induced by Ar$^+$ ion bombardment for (a) 25, (b) 35, and (c) 45 min, respectively, and (d) cross-sectional SEM image of the sample bombarded for 45 min.

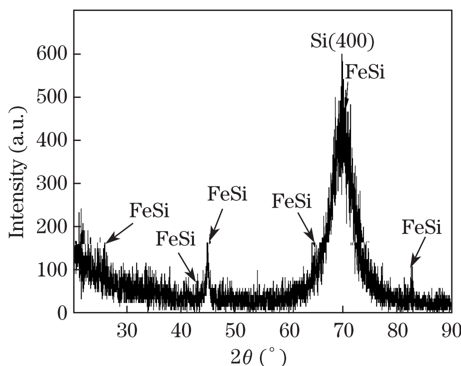

Fig. 2. XRD spectrum of a Si nanocone array.

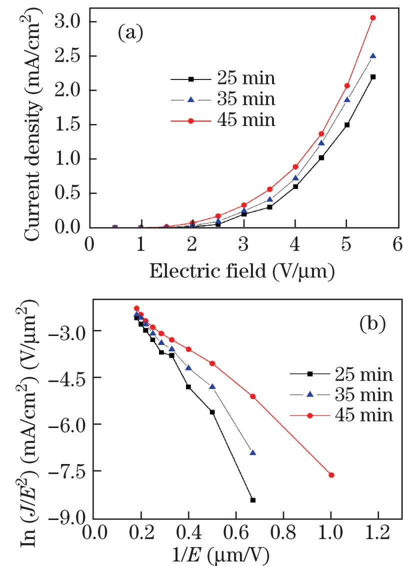

Fig. 3. (Color online) (a) Field emission $J - E$ curve and (b) corresponding FN plot of the Si nanocone arrays.

The turn-on fields of the Si nanocone arrays bombarded for 25, 35, and 45 min are 1.8, 1.7, and 1.4 V/μm, respectively. The formation of metal silicides appears to reduce the barrier height[15], which results in reductions in the turn-on field.

Figure 3(b) shows the FN plots of the Si nanocone arrays. The linearization degree indicates that emission does not originate from thermal electrons but from the field. β was calculated from the slope of the FN plot. By assuming that the Φ is ~4.15 eV for Si nanocone arrays[17], the calculated β values of the Si nanocone arrays bombarded for 25, 35, and 45 min are about 5110, 6750, and 9466, respectively. The large β observed is related to the geometric structure of the nanocone arrays.

Figure 1 shows that cones with an average height of ~460 nm, an average width of ~220 nm, and apex angles of ~24° are distributed all over the surface of the arrays. The cones have a very large curvature and length-to-diameter ratio, both of which can lead to large β. However, large β values are not absolutely dominated by the geometric structure of an array. Metal silicides formed at the apexes increase the electron density of states at the Fermi level[22]. Furthermore, the silicides contribute to decreases in the Φ[23], which is excellent for field emission. Thus, the field emission characteristics of nanocone arrays on Si substrates can be improved substantially.

Field emission J stability is an important parameter to investigate because of its vital role in field emission devices. The field emission stability of nanocone arrays is time-dependent, as shown in Fig. 4. The J was measured from 0 to 550 V at 50-V increments and 1-min intervals for a total time of 45 min. The time intervals between the forward and backward traces are 1, 5, 10, 30 s, and 1 min. One trace and retrace is shown in each plot in Fig. 4. When the interval is short (1 s), fluctuations in the field emission J are significant. Variations in the J are observed under certain E values between the forward and backward traces. At a time interval of 1 min, however, these variations become negligible, and the current densities of the forward and backward trace are nearly identical. This result could be attributed to the balance

gained between adsorption and desorption when the time interval is longer[24], which induces a more stable J.

Figure 5 shows the stability of the J of the Si nanocone array obtained by bombardment for 45 min. The J was tested under different E (0.5, 3, and 5.5 V/μm) at 1-min intervals. No fluctuations in the J under 0.5 V/μm are observed because of the absence of an emission current. Maximum fluctuations in J of about 6% and 6.2% are observed at E of 3 and 5.5 V/μm, respectively. This result demonstrates that the emission J stability fluctuates slightly and remains excellent over operational times of 24 h. Each cone presents good crystallinity[19,20], with the same crystallographic orientation on the substrate, and their structures rarely change, as indicated in the SEM image (nearly identical to Fig. 1(c)) after field emission

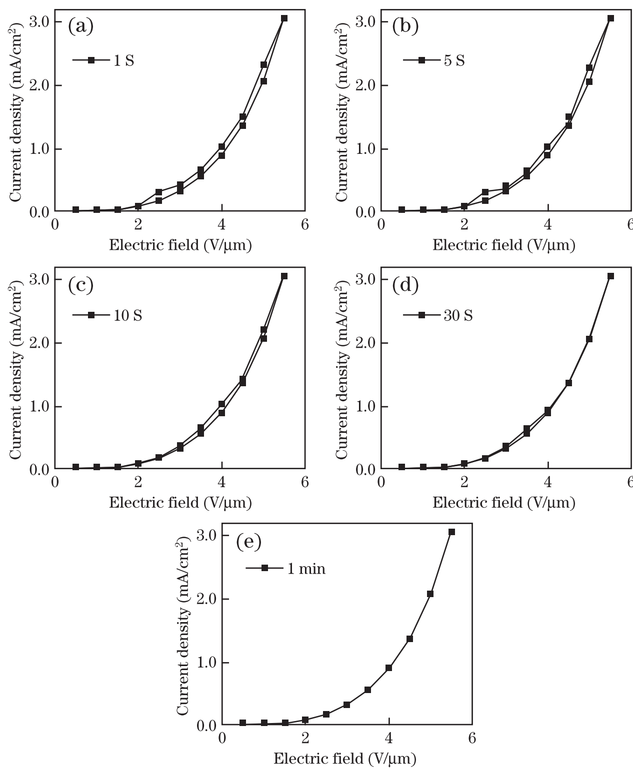

Fig. 4. $J-E$ curves of the Si nanocone arrays measured under different time intervals (1, 5, 10, 30 s, and 1 min).

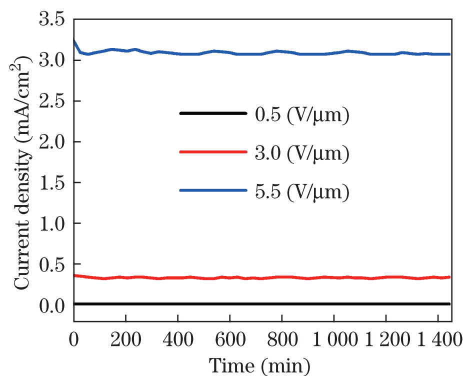

Fig. 5. (Color online) Current density stability of the Si nanocone array determined for 24 h under applied electric fields of 0.5, 3.0, and 5.5 V/μm.

for 24 h. Thus, the excellent stability of the structure of the Si nanocone array contributes to the excellent stability of the sample.

The presence of metal (Fe, Cr) silicides at the cone apex shows the following advantages: hardness close to that of diamond, high melting point (higher than 1200 °C), and high chemical stability, including anti-oxidation, no decomposition, and very little residual gas absorption. These characteristics contribute to the ultra-stable field emission current of Si nanocone arrays with metal silicides at their apexes.

In conclusion, the field emission properties of Si nanocone arrays with metal silicide (Fe and Cr)-enriched apexes are reported letter. A low turn-on field of ~1.4 V/μm and large β of ~9466 are found. Furthermore, the emission J of the array remains extremely stable for long periods of time. These excellent field emission properties suggest that the Si nanocone arrays described in this letter may be effective and reliable electron emitting sources.

This work was supported by the National Natural Science Foundation of China (Nos. 61072003, 60878044, and 60638010) and the National "973" Project of China (No. 2010CB933703).

References

1. G. Z. Yue, Q. Qiu, B. Gao, Y. Cheng, J. Zhang, H. Shimoda, S. Chang, J. P. Lu, and O. Zhou, Appl. Phys. Lett. **81,** 355 (2002).
2. H. Sugie, M. Tanemura, V. Filip, K. Lwata, K. Takahashi, and F. Okuyanma, Appl. Phys. Lett. **78,** 2578 (2001).
3. A. Haga, S. Senda, Y. Sakai, Y. Mizuta, S. Kita, and F. Okuyama, Appl. Phys. Lett. **84,** 2208 (2004).
4. Z. X. Lin and T. L. Guo, Optoelectron. Technol. **26,** 1 (2006).
5. J. F. Dai, X. W. Mu, X. T. Chen, J. H. Wang, and B. Fu, Physica E: Low-dimensional Systems and Nanostructures **44,** 152 (2011).
6. R. J. Zou, S. L. Xue, and D. Y. Li, Chin. Opt. Lett. **7,** 130 (2009).
7. W. A. Deheer, A. Chatelain, and D. Ugarte, Science **270,** 1179 (1995).
8. A. C. Dillon, K. M. Jones, T. A. Bekkedahl, C. H. Kiang, D. S. Bethune, and M. J. Heben, Nature **386,** 377 (1997).
9. N. G. Shang, F. Y. Meng, F. C. K. Au, Q. Li, C. S. Lee, I. Bello, and S. T. Lee, Adv. Mater. **14,** 1308 (2002).
10. F. Y. Meng, W. K. Wong, N. G. Shang, Q. Li, and I. Bello, Vacuum **66,** 71 (2002).
11. K. Sawada, M. Tabe, Y. Ishikawa, and M. Ishida, J. Vac. Sci. Technol. B **20,** 787 (2002).
12. H. C. Wu, H. Y. Tsai, H. T. Chiu, and C. Y. Lee, ACS Appl. Mater. Interfaces **2,** 3285 (2010).
13. J. Zhu, Z. Chen, X. Liu, J. Mu, Y. Gao, W. Han, and G. Jia, Chin. Opt. Lett. **10,** 082301 (2012).
14. Y. M. Chang, P. H. Kao, H. M. Tai, H. W. Wang, C. M. Lin, H. Y. Lee, and J. Y. Juang, Phys. Chem. Chem. Phys. **15,** 10761 (2013).
15. F. Zhao, G. A. Cheng, R. T. Zheng, D. D. Zhao, S. L. Wu, and J. H. Deng, Nanoscale Research Letters **6,** 176 (2011).
16. S. H. Yang and M. Yokoyama, Mater. Chem. Phys. **57,** 173 (1998).

17. Q. Wang, J. J. Li, Y. J. Ma, X. D. Bai, Z. L. Wang, P. Xu, C. Y. Shi, B. G. Quan, S. L. Yue, and C. Z. Gu, Nanotechnology **16,** 2919 (2005).
18. B. W. Han, J. S. Lee, and B. T. Ahn, IEEE Electron. Device Lett. **23,** 10 (2002).
19. J. Zhou, S. Facsko, M. Lu, and W. Moeller, J. Appl. Phys. **109,** 104315 (2011).
20. Y. Qiu, H. C. Hao, J. Zhou, and M. Lu, Opt. Express **20,** 22087 (2012).
21. R. H. Fowler and L. W. Nordheim, in *Proceedings of the Royal Society of London-Series A*: *Containing Papers of a Mathematical and Physical* 173 (1928).
22. S. A. Ding, Z. J. Xu, B. Q. Li, and Y. F. Zhou, Chinese Journal of Semiconductors (in Chinese) **11,** 906 (1990).
23. H. S. Uh, B. G. Park, and J. D. Lee, IEEE Electron. Device Lett. **19,** 167 (1998).
24. J. T. Chen, J. Li, J. Yang, X. B. Yan, B. K. Tay, and Q. J. Xue, Appl. Phys. Lett. **99,** 173104 (2011).