The Electron Field Emission Properties of Ag-SiO₂ Nanocomposite Layers

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ABSTRACT

In this work, Ag-SiO₂ nanocomposite layers were synthesized by introducing Ag nanoclusters into thermally oxidised SiO₂ layers, using ion implantation. The field emission (FE) properties of these layers were studied and correlated with the results from atomic force microscopy and with transmission electron microscope measurements. These nanocomposites exhibit good FE properties and give an emission current of 1 nA at electric fields as low as 13 V/μm, for a dose of $5 \times 10^{16} \text{Ag}^+/\text{cm}^2$, compared of 204 V/μm for ‘bare’ SiO₂ layers. It is clearly demonstrated that the good FE properties of these nanocomposites are attributed to two types of local field enhancement mechanisms, one due to the surface morphology and the other due to electrical inhomogeneity. The isolated conductive Ag nanoclusters embedded in the electrically insulating SiO₂ matrix provide a field enhancement due to the electrical inhomogeneity. Moreover, the implanted Ag ions were diffused to the surface, during the implantation process, and created a dense surface protrusion morphology at the surface, thus providing a geometric local field enhancement. The local field enhancement mechanisms in these samples are critically dependent on the implantation dose of Ag.

I. INTRODUCTION

Cold electron field emission (FE) materials have attracted the continuous attention of researchers, primarily due to their potential application in flat panel displays and as electron sources in vacuum microelectronic devices. Nanocomposites, containing isolated electrically-conductive clusters embedded in a relatively electrically insulating dielectric matrix¹⁻⁵, are promising candidates. They exhibit a very low threshold field, typically less than 20 V/ μm for electron emission from atomically flat surfaces, originating from the local field enhancement effects associated with the electrical inhomogeneity between the clusters and the host matrix. Various methods, such as sol-gel synthesis,⁶ co-sputtering of electrically conducting and insulating materials⁷ and metal ion implantation into a dielectric matrix,^{4,8} can be applied to synthesize the mixed phase nanocomposites. Among these methods, ion implantation has attracted significant interest due to the possibility of patterning the materials, of overcoming the doping solubility limits and of being able to introduce virtually any metallic element into any insulating matrix in accurate quantities and at fixed depths.

In this work, Ag-SiO₂ nanocomposites were synthesized by Ag implantation on SiO₂ layers, which are grown on a silicon substrate by thermal oxidation. The FE properties of these Ag-SiO₂ nanocomposites were studied and discussed in terms of their surface morphology and microstructure, as determined from atomic force microscopy and transmission electron microscopy. We use the SiO₂ as the insulating host matrix because of its excellent chemical and physical stabilities, the simple and efficient fabrication process (thermal oxidation), and the well characterised and fast etching process (HF etching). Ag is chosen for the metallic nanoclusters because it has very good electrical and thermal conductivity, which are beneficial in FE device applications. Moreover, the implanted Ag ions do not react chemically with the SiO₂ matrix^{9,10} and the formation of nano-sized pure Ag clusters in silica with small Ag doses ($1 \times 10^{15} \text{ cm}^{-2}$) has been reported.¹¹

The study of the microstructure and phase evolution of the ion-beam-synthesized metal-SiO₂ nanocomposites with various fabrication conditions has been extensively explored in the literature.⁸⁻¹² The interesting nonlinear optical properties of these layers, particularly the enhancement of the optical Kerr susceptibility, makes them interesting for optoelectronic device applications. Hence, one may apply the existing information for optimizing the fabrication parameters to achieve the desirable microstructure for FE device applications. Finally, creating the SiO₂ layer by thermal oxidation and subsequently creating the conductive clusters by metal ion implantation has the added benefit that the whole fabrication process is compatible with existing integrated circuit technology. Therefore, vacuum microelectronic devices, using these metal-SiO₂ nanocomposites as cathode material, have the advantage of possible integration with other circuit elements on a single chip.

II. SAMPLE PREPARATION AND EXPERIMENT

SiO₂ layers were grown on n-type phosphorus-doped (100) Si wafers with a resistivity $\leq 0.05 \text{ } \Omega\text{cm}$, using dry thermal oxidation at 1000 °C for 2 hours. The thicknesses of these layers were checked by ellipsometry and determined to be $120 \text{ nm} \pm 10 \text{ nm}$, over a 4 inch wafer. The resulting layers were subsequently implanted with 110 keV Ag⁺ ions at room temperature, using a 200 kV ion implanter. According to static SRIM simulation,¹³ the projected range of 110 keV Ag⁺ ions in a 110 nm-thick SiO₂ layer on a Si substrate is found to be 58 nm. The doses ranged from $1 \times 10^{16} \text{ Ag}^+/\text{cm}^2$ to $7 \times 10^{16} \text{ Ag}^+/\text{cm}^2$ and were confirmed by Rutherford backscattering spectrometry (RBS) measurements, with a 1.56 MeV ⁴He⁺ beam.

The FE properties of the samples were studied in a high vacuum chamber, with a base pressure better than $5 \times 10^{-4} \text{ Pa}$. The current-electric field (I-F) characteristics were measured using a “sphere-to-plane” electrode configuration, with a 5 mm diameter stainless-steel ball anode. The applied electric field was obtained by dividing the applied

voltage by the gap distance (typically, 40 μm). The threshold field F_{th} , is defined as the field strength where the emission current reaches 1 nA. The values of $\beta/\Phi^{3/2}$ were determined from the corresponding Fowler-Nordheim plot (not shown), where β is the field enhancement factor and Φ the tunnelling barrier (work function in the case of metal) in eV. The surface morphology was studied using atomic force microscopy (AFM). The microstructure was characterized using a Philips CM200 transmission electron microscope (TEM) (200kV accelerating voltage, LaB₆ electron source).

III. RESULTS AND DISCUSSION

The electron field emission properties as a function of Ag dose are shown in Fig. 1. The I-F characteristics of the sample with a dose of $3 \times 10^{16} \text{ Ag}^+/\text{cm}^2$ are shown in Fig. 1(a). The five successive cycle measurements taken from this sample shows a good repeatability of the I-F characteristics. The variation of F_{th} and $\beta/\Phi^{3/2}$ of the samples, with respect to the Ag dose, is shown in Fig. 1 (b). The F_{th} of the ‘bare’ SiO₂ layer decreased from 204 V/ μm to 44 V/ μm after Ag implantation to a dose of $1.0 \times 10^{16} \text{ cm}^{-2}$. The F_{th} has further decreased to 20 V/ μm when the dose of Ag was increased to $3.0 \times 10^{16} \text{ cm}^{-2}$ and attained its lowest value of 13 V/ μm at a dose of $5.0 \times 10^{16} \text{ Ag}^+/\text{cm}^2$. However, increasing the dose from $5.0 \times 10^{16} \text{ Ag}^+/\text{cm}^2$ to $7.0 \times 10^{16} \text{ Ag}^+/\text{cm}^2$ led to an increase of F_{th} to 28 V/ μm . For the ‘bare’ SiO₂ layers, the value of $\beta/\Phi^{3/2}$ was determined to be 2.0, while after Ag implantation, the values of $\beta/\Phi^{3/2}$ increased to 12.8, 22.5, 33.6 and 15.8, for the samples with doses of 1.0, 3.0, 5.0 and $7.0 \times 10^{16} \text{ Ag}^+/\text{cm}^2$, respectively.

The surface morphology of these samples was studied by AFM, and the results were shown in Fig. 2. The root mean square (r.m.s.) values of surface roughness were determined to be 0.53, 0.53, 1.1 and 6.5 nm for the samples with doses of 1.0, 3.0, 5.0 and 7.0×10^{16}

Ag^+/cm^2 , respectively. The surfaces of the three lower dose samples are very smooth, but a rougher surface, with dense surface protrusions, is achieved at the highest dose. The results of the AFM measurements are insufficient for understanding the dependence of the FE properties on the Ag dose. The highest dose sample has the roughest surface, but it does not show the lowest value of F_{th} and hence the highest value of $\beta/\Phi^{3/2}$, as would be expected from considering only the surface field enhancement model. The other three lower dose samples have smooth surfaces, but they still achieve a local field enhancement factor (β) larger than 100, if the effective barrier (Φ) is assumed to be 4.63 eV (i.e. the work function of bulk Ag).¹⁴ The FE properties of these samples can be understood if we also take into account their microstructure, together with the effect of the surface morphology.

The microstructure of these samples was studied by TEM and the results are shown in Fig. 3. As seen from the cross-sectional TEM (X-TEM) image of the lowest dose sample in Fig. 3 (a), the implanted Ag atoms exist as nano-clusters. The average diameter of these clusters is 4.8 nm and they are identified as crystalline Ag nanoparticles by high-resolution electron microscopy. A more detailed TEM study of the Ag-SiO₂ nanocomposites was reported in elsewhere.¹⁵ These isolated Ag nanoclusters are distributed through the whole SiO₂ layer, as seen from the high resolution TEM image,¹⁵ and hence create conducting paths for the emissive electrons' transportation from the substrate to the emission surface. Moreover, when an external field is present, the mobile charges in the layer will concentrate mainly at the boundaries of these localised conductive Ag clusters, due to the nature of the electrical conductivity difference between the Ag nanoclusters and SiO₂ matrix. The electric field lines will terminate at the mobile charge. This leads to a local electric field enhancement due to the electrical inhomogeneity. Hence, the F_{th} of the 'bare' SiO₂ layer decreased from 204 V/ μm to 44 V/ μm after Ag implantation of a dose of $1.0 \times 10^{16} \text{ Ag}^+/\text{cm}^2$, although the Ag implanted layer has an atomically smooth surface. As shown in Fig. 3 (b), when the Ag dose is increased,

the concentration of the Ag clusters is also increased. Moreover, more Ag nanoclusters appeared at the emission surface, because of the diffusion of Ag atoms during implantation. Hence, F_{th} further decreased to 20 V/ μ m when the dose of Ag was increased to 3.0×10^{16} Ag⁺/cm², and attained its lowest value of 13 V/ μ m at a dose of 5.0×10^{16} Ag⁺/cm², with an increased number of field emission sites and the number of emission conducting paths.

However, by further increasing the Ag dose, the Ag clusters coalesced together to form large clusters, which finally led to the creation of an relatively continuous layer, as shown in X-TEM image of the highest dose sample in Fig. 3 (c). Hence, the local field enhancement due to the electrical inhomogeneity effect decreased. At the same time, more Ag atoms diffused to the surface from the projected range region with increasing of the Ag dose, as observed from the X-TEM images in Fig. 3. This is caused by Ag⁺ being a fast-diffusing atom in the SiO₂ matrix¹⁶, and because of the ion beam-assisted heating during implantation enhancing the diffusion process, becoming more significant with increasing the dose. Therefore, a dense surface-protrusion structure was formed in the highest dose sample as shown in Fig. 2 (d). The dense surface-protrusion structure provides a geometric local field enhancement for the highest dose sample, which goes towards balancing the decreased contribution of the electrical inhomogeneity field enhancement. Hence, F_{th} increases to 28 V/ μ m from the optimized value of 13 V/ μ m when the dose increases from 5.0×10^{16} Ag⁺/cm² to 7.0×10^{16} Ag⁺/cm². However, this is still better than the value of 44 V/ μ m of the lowest dose sample, which has a smooth emission surface and a small amount of isolated Ag nanoclusters.

IV. CONCLUSION

In summary, the synthesis process and FE properties of Ag-SiO₂ nanocomposite layers, which are potential candidates for FE device applications, were reported. These nanocomposites were synthesized by Ag implantation on thermally-oxidised SiO₂ layers and

the whole process is compatible with exiting integrated circuit technology. Moreover, they exhibit good FE properties, with threshold fields as low as 13 V/ μm with a dose of 5×10^{16} Ag⁺/cm². The FE mechanisms of these layers were discussed and associated with two types of local enhancement mechanism, namely due to the electrical inhomogeneity between the Ag clusters and the SiO₂ matrix and the morphology of the emitting surface.

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Reference:

1. O. Gröning, O.M. Küttel, P. Gröning and L. Schlaphach, Appl. Surf. Sci. 111, 135 (1996).
2. A. Ilie, A.C. Ferrari, T. Yagi, J. Robertson, Appl. Phys. Lett. 76, 2627 (2000).

3. J.D. Carey, R.D. Forrest, R.U.A. Khan, S.R.P. Silva, Appl. Phys. Lett. 77, 2006 (2000).
4. W.M. Tsang, S.P. Wong and J.K.N. Lindner, Appl. Phys. Lett. 81, 3942 (2002).
5. N.S. Xu and S. Ejaz Huq, Mater. Sci. & Eng. R27, 47 (2005).
6. G. De, A. Licciulli, C. Massaro, L. Tapfer, M. Catalano, G. Battaglin, C. Meneghini and P. Mazzoldi, J. Non-Cryst. Solids 194, 225 (1996).
7. D. Boscarino, A. Vomiero, G. Mattei, A. Quaranta, P. Mazzoldi, and G. D. Mea, J. Vac. Sci. Technol. B 23, 11 (2005).
8. G. W. Arnold and J. A. Borders, J. Appl. Phys. 48, 1488 (1977).
9. E. Cattaruzza, Nucl. Instr. and Meth. B 169, 141 (2000).
10. G. Battaglin, Nucl. Instr. and Meth. B 116, 102 (1996).
11. N. Arai, H. Tsuji, M. Motono, Y. Gotoh, K. Adachi, H. Kotaki and J. Ishikawa, Nucl. Instr. and Meth. B 206, 629 (2003).
12. P. D. Townsend, Rep. Prog. Phys. 50, 501 (1987).
13. www.srim.org
14. R. C. Weast, CRC Handbook of Chemistry and Physics, 81th ed., Chemical Rubber, Boca Raton, FL, (2000-2001)
15. W.M. Tsang, V. Stolojan, S. P. Wong, B. J. Sealy and S. R. P. Silva, Mater. Sci. & Eng. B (submitted).
16. J.F. McBrayer, R.M. Swanson, T. W. Sigmon and J. Bravman, Appl. Phys. Lett. 43, 653 (1983).

Figure Captions

Fig. 1 Field emission properties of the Ag-SiO₂ nanocomposite layers. (a) I-F characteristics

from five successive cycles of the sample with a dose of $3 \times 10^{16} \text{ Ag}^+/\text{cm}^2$; (b) The variation of F_{th} and $\beta/\Phi^{3/2}$ against Ag dose, showing the best candidate for FE applications at an implantation dose of $5 \times 10^{16} \text{ Ag}^+/\text{cm}^2$.

Fig. 2 AFM micrographs showing the surface morphology of the samples with various Ag dose (a) $1 \times 10^{16} \text{ Ag}^+/\text{cm}^2$; (b) $3 \times 10^{16} \text{ Ag}^+/\text{cm}^2$; (c) $5 \times 10^{16} \text{ Ag}^+/\text{cm}^2$; (d) $7 \times 10^{16} \text{ Ag}^+/\text{cm}^2$. The x- and y- scales are 1 mm/div and the z-scale is 40 nm/div in all the three micrographs.

Fig. 3 Bright field X-TEM micrographs of the samples implanted with various Ag dose (a) $1 \times 10^{16} \text{ Ag}^+/\text{cm}^2$; (b) $5 \times 10^{16} \text{ Ag}^+/\text{cm}^2$; (c) $7 \times 10^{16} \text{ Ag}^+/\text{cm}^2$. As the implantation dose increases, the Ag nano-crystallites (Fig. 3a) begin to coalesce (Fig. 3b), ultimately leading to the larger crystallites dominating the microstructure and protruding out of the emitting surface (Fig. 3c).

Figure 1
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Figure 2
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Figure 3
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