The Structural and Electron Field Emission Properties of Ion-Beam-Synthesised Metallic-Dielectric Nanocomposites


Nanoelectronics Centre, Advanced Technology Institute, School of Electronics and Physical Sciences, University of Surrey, Guildford, GU2 7XH, United Kingdom
Department of Electronic Engineering, Chinese University of Hong Kong, Hong Kong
Universität Augsburg, Institut für Physik, D-86135 Augsburg, Germany

Abstract

Metallic-dielectric nanocomposites, including Ag-SiO$_2$, Co-SiO$_2$ and WC-SiC, were synthesised on silicon substrates using ion implantation. The electron field emission (FE) properties of these nanocomposites were studied and correlated to their microstructure determined from the measurements of atomic force microscopy, Rutherford backscattering spectroscopy, x-ray photoelectron spectroscopy and transmission electron microscopy. These nanocomposites exhibit excellent FE properties and give an emission current of 1 nA at the applied electric fields as low as 5 V/$\mu$m for Co-SiO$_2$ nanocomposite layers. Moreover, the results are clearly shown that isolated metallic clusters embedded in a relatively electrically insulating matrix can create local field enhancement on the samples attributed to the electrical inhomogeneity effect.
1. **INTRODUCTION**

Metallic nanoclusters embedded in dielectric matrices (i.e. metallic-dielectric nanocomposites) have attract a significant research interest from the community over several decades because of their uniquely optical and magnetic properties. For instance, metal nanoclusters embedded in the glass matrix exhibit an enhanced optical Kerr susceptibility and picosecond response time thus make them interesting for optoelectronic device application [1, 2]. Furthermore, isolated ferromagnetic nanoparticles embedded in the dielectric are the promising candidate for next generation ultra-high-density magnetic data storage [3, 4]. In this work, we shall demonstrate that metallic-dielectric nanocomposite layers have excellent field emission (FE) properties. Electrons can be easily extracted out from their surface to vacuum under relatively low electric fields ($\leq 20$ V/$\mu$m) by the electron FE process when compared with several thousand volts per micrometer for the flat metallic cathodes. This is originating from the local field enhancement associated with the electrical inhomogeneity between the metallic nanoclusters and the host matrix [5-8].

In this work, metallic-dielectric nanocomposites were synthesised on silicon (Si) substrates using ion implantation technique. In comparison of other fabrication techniques such as sol-gel synthesis and sputtering, 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 dielectric matrix in accurate quantities and at fixed depths. At first, either thermally oxidised silicon oxide (SiO$_2$) layers or ion-beam-synthesised silicon carbide (SiC) layers were growth on Si substrates. Implantation of silver (Ag), cobalt (Co) or tungsten (W) ions was sequentially performed on these dielectric layers to create Ag-SiO$_2$, Co-SiO$_2$ and WC-SiC nanocomposites.

We use the SiO$_2$ 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 and Co chosen for the metallic
nanoclusters in the SiO$_2$ because they do not react chemically with the SiO$_2$ matrix and the formation of nano-sized pure Ag and Co clusters in silica are reported [9, 10]. On the other hand, SiC is a promising wide band-gap semiconductor material with a number of attractive properties such as high electron mobility, high thermal conductivity, and excellent physical and chemical stability [11]. W was chosen to implant to SiC layer because it is a carbide forming element and tungsten carbide (WC) is known to exhibit n-type metallic conduction with an electrical resistivity lower than 17 $\mu\Omega$·cm [12] and a work function of 3.6 eV [13]. Moreover, WC is also thermally, physical and chemically stable.

2. Sample Preparation and Experiments

The substrates used in this work are n-type (100) Si wafer with resistivity less than 0.05 $\Omega$·cm. SiO$_2$ layers were thermal growth on the substrate by dry oxidation at 1000 °C. The thicknesses of SiO$_2$ layers for the Ag and Co ion implantation were 120 and 150 nm, respectively. The Ag and Co ion implantations were preformed using a conventional high current implanter to a fixed dose of $5 \times 10^{16}$ ions/cm$^2$. The implantation energy is 110 keV for Ag$^+$ and is 50 keV for Co$^+$. The projected range of 110 keV Ag$^+$ ions and 50 keV Co$^+$ is found to be 58 nm and 45 nm, respectively, by SRIM simulation [14].

The SiC layers used for W implantation were synthesised by high dose carbon implantation to a dose of $0.8 \times 10^{18}$ cm$^{-2}$ into Si wafers using a metal vapor vacuum arc (MEVVA) ion source. The carbon plasma in MEVVA ion sources contains almost exclusively singly charged ions [15]. The details of the fabrication of the ion-beam-synthesised SiC layers were reported elsewhere [7]. Resulting layers were subsequently implanted with W ions at 70 kV using a fixed dose of $1 \times 10^{17}$ ions/cm$^2$. The W plasma contains ions of charge states 1$^+$ to 6$^+$ with particle current fractions as reported in [15]. These results in W ions with an energy of up to 420 keV, leading to a SRIM predicted range distribution peaking at 60 nm and with a lower wing extending down to 180 nm.

The implantation doses were confirmed by Rutherford backscattering spectrometry
(RBS) measurements, with a 1.56 MeV \(^4\)He\(^+\) beam. The surface morphology was studied using atomic force microscopy (AFM). The microstructure was characterized using a transmission electron microscope (TEM). The chemical bonding conditions were studied by x-ray photoelectron spectroscopy (XPS). The FE properties of the Ag-SiO\(_2\) and Co-SiO\(_2\) samples were measured using a “sphere-to-plane” electrode configuration, with a 5 mm diameter stainless-steel ball anode in a high vacuum chamber (\(\leq 5\times10^{-4}\) Pa) [6]. The anode was mounted on a Vacuum Generator HPT translator, which allowed FE maps to be carried out without the need for the sample to be returned to atmosphere. The applied electric field was obtained by dividing the applied voltage by the gap distance (typically, 50 \(\mu\)m). Alternatively, the FE properties of the W-SiC samples were measured using a ‘parallel plane’ electrode configuration with a copper plate as the anode in an ultra-high vacuum chamber (\(\leq 3\times10^{-6}\) Pa) [7]. The separation between the sample surface and the Cu anode was 25 \(\mu\)m using a mica spacer and the emission area was about 0.3 cm\(^2\). Hence, the current density field (J-E) characteristics of the samples could be achieved.

3. RESULTS AND DISCUSSION

3.1 Ag-SiO\(_2\) and Co-SiO\(_2\) nanocomposites

The surface of the Ag-SiO\(_2\) and Co-SiO\(_2\) nanocomposite layers is very smooth as shown in AFM measurements (not shown). The root-mean-square (rms) values of surface roughness were determined to be 1.1 and 0.5 nm for Ag-SiO\(_2\) and Co-SiO\(_2\) nanocomposite layers, respectively. Hence, these layers are lack of surface protrusions structure to provide significantly geometric local enhancement. The microstructure of these layers was studied by TEM. The cross-sectional TEM (XTEM) micrographs are shown in Fig. 1 and the statistical distribution of the metallic clusters size determined from the XTEM measurements are shown in Fig. 2.

Both of the implanted Ag and Co ions exist as nanoclusters in the SiO\(_2\) layers and these
nanoclusters are identified as crystalline metal nanoparticles by high-resolution TEM and XPS measurements. However, the sizes and the distributions of the implanted metal clusters are very different in these two samples. As shown in Fig. 2, relatively wide cluster size distribution is observed in the Ag implanted sample and the cluster sizes are ranging from 2 to 20 nm in diameter. Near to the surface, the size of the Ag clusters is ~ 2-3 nm and which is acted as emission sites for the FE process. As the depth from surface is increased, the size and concentration of the Ag clusters also increases. Ag clusters with sizes of ~ 9 nm, are located at a depth of 50 nm beneath the surface, which is close to the project range predicted by SRIM. Finally, the Ag clusters with a maximum size of 20 nm are located at a depth of 80 nm beneath the surface. On the other hand, the Co implanted sample has a narrow cluster size distribution and the size of the clusters is much smaller that of the Ag implanted sample on average as shown in Fig. 2. The sizes of the Co nanoclusters are determined to be ~ 3.6 nm on average and the maximum size of the Co nanoclusters is less than 7 nm as compared with 20 nm of Ag nanoclusters. Besides, Co nanoclusters are only appeared in a depth up to ~ 100 nm beneath the surface, in contrast to the Ag implanted layer where Ag nanoclusters exist in the whole SiO₂ layer.

The 50 nm thick Co deficient SiO₂ layer in the Co-implanted sample will prevent electrons transporting from substrate to the vacuum during the electron FE process. Hence, in contrast to the conventional bottom electrical contact used in the Ag implanted sample in the FE measurement, surface electrical contact was employed in the Co implanted sample. Thus allowing the electrons to flow through the conducting surface to emission sites and be emitted to the extraction electrode. The electron FE properties of these metal implanted SiO₂ layers are shown in Fig. 3. From current-field (I-F) characteristics shown in Fig. 3a, the threshold fields (Fₜₜₜ), which is defined as the field strength where the emission current reaches 1 nA, are determined to be 13 and 5 V/μm for the Ag and Co implanted samples, respectively.

The I-F characteristics of ‘bare’ SiO₂ layers are also measured as control experiments
(not shown) and the $F_{th}$ are determined to be $\sim 200$ V/$\mu$m. Moreover, high-field conditioning took part in the FE process of the ‘bare’ SiO$_2$ layers to create conductive paths for transporting the emissive electrons by dielectric breakdown and led to surface destructions. However, the conditioning process is absent in the metal implanted layers because metallic nanoclusters within the SiO$_2$ layers can directly provide conductive paths for emissive electrons, hence, avoid the surface destruction. Moreover, when an external field is present, the mobile charges in the layers will concentrate mainly at the boundaries of the localised metallic nanoclusters, due to the nature of the electrical conductivity difference between the metallic nanoclusters and the SiO$_2$ matrix. The electric field lines will terminate at the mobile charge. This leads to a local electric field enhancement due to the electrical inhomogeneity [5-8], and hence, improves the $F_{th}$ of the ‘SiO$_2$’ layers from $\sim200$ V/$\mu$m to 12 and 5 V/$\mu$m after implantation of Ag and Co ions, respectively.

3.2 WC-SiC nanocomposites

At first, a uniform 160 nm thick amorphous SiC layer was achieved by carbon implantation. After tungsten implantation to a dose of $1 \times 10^{17}$ cm$^{-2}$, WC nanoclusters were formed with an average size of several nanometres, revealed themselves as dark dots in the XTEM micrograph as shown in Fig 1c. That these dark dots were indeed WC was confirmed by XPS measurements. The surface of the layer before and after W implantation is also atomically smooth (r.m.s < 0.5 nm) as shown in the AFM measurements. However, the turn-on field $F_{on}$, which is defined as the field strength where the emission current density reaches 1 $\mu$A/cm$^2$, is decreased from 25 to 14 V/mm after W implantation (Fig. 3b). Therefore, it is evident that the metallic WC clusters do also lead to local field enhancement and provide conducting paths for the emissive electron in the SiC layer similar to the metal nanoclusters in the SiO$_2$ layers.

In comparison of SiO$_2$, the SiC have an advantage of its excellent thermal conductivity
and which is beneficent in the field emission device in term of stability. However, the SiO$_2$
has a more effective etching process (HF etching) and which is useful for patterning the
device structure.

IV. CONCLUSION

In summary, the fabrication process of Ag-SiO$_2$, Co-SiO$_2$ and WC-SiC nanocomposites
are reported. Their electron field emission properties are studied and are discussed in
conjunction with their structural properties determined from measurements of AFM, TEM and
XPS. Results indicate clearly that metallic-dielectric nanocomposite layers have achieved
excellent FE properties with $F_{th}$ as low as 5 V/µm. The good FE properties of these layers are
attributed to electrical inhomogeneity local field enhancement effect due to embedded
metallic nanoclusters.

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Reference


Figure Captions

Fig. 1  Bright-field XTEM micrographs of the samples with implantation of (a) Ag ions on SiO₂ layer, (b) Co ions on SiO₂ layer and (c) W ions on SiC layer.

Fig. 2  The statistical distribution of metallic clusters within the samples with implantation of (a) Ag ions on SiO₂ layer and (b) Co ions on SiO₂ layer, as derived from XTEM.

Fig. 3  The I-F characteristics of the samples with (a) Ag and Co implanted SiO₂ layers using “sphere-to-plane” electrode configuration and (b) W implanted SiC layer using “parallel plane” electrode configuration.
Figure 1
Figure 3