Electron field emission properties of Co quantum dots in SiO_2 matrix synthesised by ion implantation

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ABSTRACT

In this work, Co ions were implanted onto thermally oxidised SiO_2 layers on silicon substrates. The implantation energy was 50 keV and the doses were 1, 3, 5 and 7×10^{16} Co^+/cm^2. The field emission (FE) properties of these layers were studied and correlated with results from atomic force microscopy and transmission electron microscopy measurements. Except for the lowest dose sample, crystallised Co nanoclusters, with size ranging from 1.8 to 5.7 nm, are observed in these Co implanted layers. The higher dose samples exhibit excellent FE properties and give an emission current of 1 nA at electric fields as low as 5 V/μm, for a dose of 5×10^{16} Co^+/cm^2 compared with 120 V/μm for the lowest dose samples. It is clearly demonstrated that the excellent FE properties of these layers are attributed to the formation of Co nanoclusters as the electrical inhomogeneity local field enhancement effect. Finally, repeatable staircase current-field (I-F) characteristics were observed in FE measurements of these higher dose samples as compared to conventional Fowler-Nordheim type I-F characteristics in lowest dose sample. It is possibly attributed to Coulomb blockade effect arising from the isolated metal quantum dots.

1. INTRODUCTION

Nanostructured materials not only have unique physical and chemical properties but also show excellent and interesting electron field emission (FE) properties. Although, the FE mechanisms of the nanostructured materials are still under investigation, their physically confinement structures play an important role on it. Ultra-thin dielectric coatings on the emitter and quantum well FE structure show resonant tunnelling characteristics in their FE measurements attributed to two-dimensional electron confinement effect [1-4]. Furthermore, one-dimensional nanostructure such as carbon nanotubes and various types of nanowires achieve an emission current at extremely low applied electric fields (typically less than 5 V/μm) [5-7]. Hence, it is of great practical and scientific interest to study the FE properties of zero dimension materials.

Metallic quantum dots embedded in dielectric matrices exhibit promising nonlinear optical properties, particularly the enhancement of the optical Kerr susceptibility, and interesting magnetic properties such as super-paramagnetic effect because of their zero dimensionally physical structure [8-10]. Ion implantation is an attractive technique for the synthesis of metallic nanoclusters in dielectric matrices due to the possibility of being able to introduce virtually any metallic element into any dielectric matrix in accurate quantities and at fixed depths. Recently, the FE properties of Ag nanoclusters embedded in SiO_2 matrix synthesised by ion implantation are reported and the results are promising [11]. They give an emission current with applied electric fields less than 20 V/μm and their fabrication process is fully compatible with the integrated circuit technology.

In this work, Co ions were implanted onto thermally oxidised SiO_2 layers on silicon substrate to synthesise Co quantum dots. The Co ion does not react chemically with SiO_2 matrix and has a small diffusion coefficient in SiO_2 matrix as compared to the Ag ion [12], hence, small sized Co nanoclusters, with narrow size dispersion, are achieved and is desirable for the study the FE properties of the metal quantum dots. Excellent FE properties, with threshold fields as low as 5 V/μm, and repeatable staircase-like I-F characteristics are achieved in these samples.

2. SAMPLE PREPARATION AND EXPERIMENTS

SiO_2 layers were grown on n-type phosphorus-doped (100) Si wafers with a resistivity ≤ 0.05 Ωcm, using dry thermal oxidation at 1000 °C for 2.5 hours. The resulting layers were subsequently implanted with 50 keV Co^+ ions at room temperature, using a 200 kV ion implanter. According to static SRIM simulation [13], the projected range of 50 keV Co^+ ions in a 150 nm-thick SiO_2 layer on a Si substrate is found to be 43 nm. The doses ranged from 1×10^{16} Co^+/cm^2 to 7×10^{16} Co^+/cm^2 and were confirmed by Rutherford backscattering spectrometry (RBS) measurements, with a 1.56 MeV $^4He^+$ beam. 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, LaB_6 electron source).

The FE properties of the samples were studied in a high vacuum chamber, with a base pressure better than 5×10^{-4} 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. Topside electrical contacts to the sample surface were employed, thus allowing the electrons to flow through the conducting surface to emission sites and be emitted to the extraction electrode. The applied electric field was obtained by dividing the applied voltage by the gap distance (typically, 100 μm). The threshold field F_{th}, is defined as the field strength where the emission current reaches 1 nA. The measurement was performed at several different regions in each sample and the high voltage is stepped up and down for three times to check the repeatability and homogeneity.

3. RESULTS AND DISCUSSIONS

The surface of these Co implanted SiO_2 layers is atomically smooth as determined from AFM measurements. The root-mean-square (rms) values of surface roughness were determined to 0.4, 0.4, 0.2 and 0.5 nm for the samples with doses of 1, 3, 5 and 7×10^{16} Co^+/cm^2, respectively. Hence, the geometric local field enhancement effect is negligible in these samples. The microstructure of these samples was studied by TEM. The cross-sectional TEM (XTEM) images are shown in Fig. 1 and the statistical distribution of the Co nanoclusters sizes are shown in Fig 2.

Except for the lowest dose (1×10^{16} Co^+/cm^2) sample, nanoclusters are observed in the SiO_2 layer and are identified as crystalline Co nanoparticles from high resolution TEM image. The average size, d, of these Co nanoclusters are determined to be 1.8, 3.6 and 5.7 nm in diameter for the samples with doses of 3, 5 and 7×10^{16} Co^+/cm^2, respectively. The corresponding statistical standard derivations, Δd, of the clusters sizes are determined to be 0.8, 0.9 and 1.2 nm for the samples with doses of 3, 5 and 7×10^{16} Co^+/cm^2, respectively. As compared to the Ag implanted SiO_2 layers, in which the d and Δd is determined to be 6.2 nm and 2.5 nm for the sample with a dose of 3×10^{16} Co^+/cm^2, the Co implanted SiO_2 layers have small and narrow distributed metal clusters. On the other hand, the implanted Co ions are seen to dissolve in the SiO_2 matrix for the lowest dose sample. Only very little amounts of Co nanoclusters with size of up to 2 nm are observed in the region located at a depth of 40 nm beneath the surface and HRTEM images fail to indicate any lattice fringes in the nanoclusters.

The electron field emission characteristics of these Co-implanted samples are shown in Fig. 3 and Fig. 4. High field conditioning process is required for the lowest dose sample to achieve stable emission current. Moreover, surface destructions are resulted after the conditioning process. The F_{th} of lowest dose sample after the conditioning process is 120 V/μm and its I-F characteristic obey the Fowler-Nordheim (FN) tunnelling mechanisms as shown in the corresponding FN plots (Fig. 4). These results suggest that dielectric breakdown was occurred during FE emission process to create conductive channels for further electron emission, similar to the early observation of pre-breakdown current study in oxide covered metal cathode [14].

In contrast to the lowest dose sample, conditioning processes are absent from the other three higher dose samples because the Co nanoclusters in these samples have provided conductive channels for the emissive electrons instead of the creation of conductive channels by dielectric breakdown. However, I-F characteristics of these higher dose samples cannot be fully described by the FN tunnelling process because non-linear FN plots are observed in Fig. 4. The FN plots of the sample with a dose of 3×10^{16} Co^+/cm^2 can be divided into 3 line segments and saturation in emission current at field strength between 70 and 96 V/μm observed in Fig 3 (a). The presence of three line segments in FN plots are commonly observed in carbon nanotubes and possibly can be explained by space charge effects or surface adsorbate effects [15].

However, two steps staircase-like I-F characteristics of two steps are observed in the two highest dose samples (5 and 7×10^{16} Co^+/cm^2) and are repeatable in the three successive measurements as shown Fig. 3. The width of staircase is roughly constant, and, is determined to be values of 1.5 and 5.0 V/μm for the samples with doses of 5 and 7×10^{16} Co^+/cm^2, respectively. The staircase current-voltage (IV) characteristics are observed in the metal implanted SiO2 layers even at room temperature attributed to the Coulomb blockage effect arising from the metal quantum dots [16]. Moreover, staircase I-F characteristics are theoretically predicted for the metal quantum dots [17]. Although, the fluctuation in size and separation of the metal clusters trend to average out effects due to single charge tunnelling, the FE currents are often expected to be dominated by a group of emission sites which have the lowest F_{th}. The F_{th} of the Co quantum dots is expected to be dependent on the size of dots and separation among the dots, hence, the FE current from these samples is mainly contributed by a group of Co quantum dots with certain size and separation. Hence, the observation of the staircase I-F characteristics in these Co implanted samples could be attributed to the Coulomb blockage effect arising from Co quantum dots, although, a more detail study is required to confirm this phenomenon.

On the other hand, the dependences of the implantation dose on the F_{th} of these Co implanted layers are consistent with the observations made with Ag implanted SiO_2 layers and can be qualitatively understood by electrical inhomogeneity effect. The isolated Co nanoclusters embedded in SiO_2 matrix create conductive paths for the emissive electrons transporting from the source to the emission surface, therefore, the formation of conductive paths by dielectric breakdown can be avoided. Moreover, when an external field is present, the mobile charges in the layer will concentrate mainly at the boundaries of these localised conductive Co nanoclusters, due to the nature of the electrical conductivity difference between the Co 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.

Hence, the F_{th} decreased from 120 V/μm to 50 V/μm after the appearance of significant amount of Co nanoclusters when the dose increased from 1 to 3×10^{16} Co^+/cm^2 as observed in XTEM images in Fig. 1. When the Co dose is increased, the concentration of the Co clusters is also increased; hence, F_{th} further decreases to 5 V/μm, with an increased number of field emission sites and the number of emission conducting paths. However, by further increasing the Co dose, the local field enhancement on the Co nanoclusters are decreased attributed to adjacent field screening effect as the Co nanoclusters are densely packaged in the SiO_2 layers . Hence, the F_{th} slightly increase from 5 V/μm to 12 V/μm for the highest dose sample.

CONCLUSIONS

In short, the fabrication and electron field emission properties of Co quantum dots embedded in SiO_2 matrix by ion implantation are reported. These samples show excellent FE properties with threshold fields as low as 5 V/µm and is comparable to other popular FE materials. The structures of these samples were studied by AFM, RBS and TEM. The excellent FE properties of these samples are discussed in term of electrical inhomogeneity effect attributed to the isolated Co nanoclusters embedded in the electrically insulating SiO_2 matrix. Finally, interesting staircase I-F characteristics are observed in the samples with appropriate implantation dose and could be attributed to the Coulomb blockage arising from the Co quantum dots.

ACKNOWLEDGMENTS

W.M. Tsang would like to acknowledge the financial support from the Croucher Foundation. The financial support from the EPSRC in the form of a Portfolio Partnership Award is gratefully acknowledged. This work is also partially supported by the Research Grants Council of Hong Kong SAR (ref. no.: CUHK4200/01E).

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Figure Captions

Fig. 1 Bright-field XTEM micrographs of the samples implanted with doses of (a) 1×10^{16} Co^+/cm^2, (b) 3×10^{16} Co^+/cm^2, (c) 5×10^{16} Co^+/cm^2 and (d) 7×10^{16} Co^+/cm^2.

Fig. 2 The statistical distribution of Co clusters within the samples with doses of of (a) 3×10^{16} Co^+/cm^2, (b) 5×10^{16} Co^+/cm^2 and (c) 7×10^{16} Co^+/cm^2.

Fig. 3 The I-F characteristics from three successive measurements of the samples implanted with a doses of (a) 1 and 3×10^{16} Co^+/cm^2, (b) 5×10^{16} Co^+/cm^2 and (c) 7×10^{16} Co^+/cm^2 with emission current in log scale. The inserts in (a) shows the experimental arrangement of the I-F measurements, (b) and (c) are the corresponding I-F plots with linear scale in emission current.

Fig. 4. The FN plots of the samples implanted with a doses of (a) 1 and 3×10^{16} Co^+/cm^2, (b) 5×10^{16} Co^+/cm^2 and (c) 7×10^{16} Co^+/cm^2.