The dielectric properties of Co-implanted SiO₂ investigated using spatially-resolved EELS

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Summary: Metallic quantum dots implanted in a silicon dioxide thin layer, grown on a silicon substrate, show promising field emission properties, giving an emission current of 1nA at electric fields as low as 5V/ μ m. This value is achieved for an implantation dose 5×10^{16} ions/cm², compared to 120 V/ μ m for the lowest dose. Electron microscopy reveals that the Co dots form metallic spheres, with a narrow diameter distribution (1-5nm). Increasing the dose to 7×10^{16} ions/cm² increases the field emission threshold. Using energy loss spectroscopy with high spatial resolution, we analyse the dielectric properties across the implanted layers in terms of effective media theories. Finally, repeatable staircase current-field characteristics were observed in field emission measurements of the higher dose samples, when compared to the characteristic Fowler-Nordheim behaviour in the lower dose samples.

1 Introduction

Nanostructured materials show excellent and interesting electron field emission (FE) properties. Although the FE mechanisms of nanostructured materials are still under investigation, their physically-confined structures play an important role in it. Ultra-thin dielectric coatings on the emitter and quantum well FE structures show resonant tunnelling characteristics in their FE measurements, attributed to two-dimensional electron confinement [1]. Furthermore, one-dimensional nanostructures, such as carbon nanotubes and various types of nanowires, achieve an emission current at extremely low applied electric fields (typically less than 5 V/ μ m) [2]. 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 [3]. 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. In this work, Co ions were implanted onto thermally oxidised SiO₂ layers on silicon substrate to synthesise Co quantum dots. The Co ion does not react chemically with the SiO₂ matrix and has a small diffusion coefficient in SiO₂ matrix as compared to the Ag ion [4]; thus, small-sized Co nanoclusters with narrow size dispersion are obtained. Excellent FE properties, with threshold fields as low as 5 V/ μ m, and repeatable staircase-like I-F characteristics are achieved in these samples.

2 Experimental Details

2.1 Sample Preparation

SiO₂ layers were grown on n-type phosphorus-doped (100) Si wafers 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. The projected range of 50 keV Co⁺ ions in a 150 nm-thick SiO₂ layer on a Si substrate is found using static Stopping and Range of Ions in Matter (SRIM) simulations to be 43 nm. The doses ranged from 1×10^{16} Co⁺/cm² to 7×10^{16} Co⁺/cm² and

were confirmed by Rutherford backscattering spectrometry (RBS) measurements, with a 1.56 MeV $^4\text{He}^+$ beam. Cross-sectional electron microscopy samples were prepared by mechanical grinding and polishing followed by ion beam thinning using a Gatan Precision Ion Beam Polisher.

2.2 Instrumentation and Analysis.

The samples were analysed using a Philips CM200 TEM (LaB₆ filament, 200keV) fitted with a Gatan Imaging Filter, employing energy loss spectroscopic profiling (ELSP) and in a dedicated Scanning Transmission Electron Microscope (STEM- Hitachi HD2300A, Schottky field emission, 200keV) fitted with a Gatan Enfina spectrometer. Low loss spectra were collected across the SiO₂ layers and the plasmon energy was measured as a function of position across the implanted layers using a modified Lorentzian function. Experimental dielectric functions were extracted from spectra collected from pure SiO₂ and Co samples, using Kramers-Kronig analysis. 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. The threshold field F_{th} , is defined as the field strength where the emission current reaches 1 nA.

3 Results

3.1 Characteristics and Field Emission Properties of the Implanted Layers.

Figure 1 shows histograms representing the distribution of Co particle diameters in the implanted layers. The distributions are relatively narrow when compared to the other material of choice for implantation for field emission applications, Ag. The average diameter increases from 1.8 nm at $3 \times 10^{16} \text{ Co}^+/\text{cm}^2$ to 3.6 nm at $5 \times 10^{16} \text{ Co}^+/\text{cm}^2$ and to 5.7 nm at $7 \times 10^{16} \text{ Co}^+/\text{cm}^2$. As the surface of these Co implanted SiO₂ layers is atomically smooth, as verified from AFM measurements, surface-geometry field enhancement can be neglected. For the sample implanted at a dose of $1 \times 10^{16} \text{ Co}^+/\text{cm}^2$, field emission is obtained after high-voltage conditioning, which creates conductive channels through dielectric breakdown; this was not necessary for the higher dose samples. The measured

threshold field was 120 V/μm. As the dose increases to $3 \times 10^{16} \text{ Co}^+/\text{cm}^2$, the threshold field drops to 50 V/μm and further drops to 5 V/μm for the $5 \times 10^{16} \text{ Co}^+/\text{cm}^2$ implantation dose. Increasing the dose again to $7 \times 10^{16} \text{ Co}^+/\text{cm}^2$ slightly raises the threshold field to 12 V/μm [5]. In order to understand the relationship between the threshold field and the diameter and concentration of Co particles, we look to spatially-resolved low-energy loss spectra in order to assess changes in the dielectric function caused by the quantum confinement of the Co clusters and the screening between adjacent clusters with increasing dose.

3.2 Effective media dielectric theories.

These theories are based on the derivation of an effective dielectric function (ϵ_{eff}) that describes the behaviour of the composite medium [6]. The first of these theories is simple averaging of the dielectric functions for a media composed from two dielectrics, A and B. This works well for alloys, at least to a first approximation. Accounting for some inter-particle interactions, the Maxwell-Garnett theory is restricted to small particles of the dielectric A (ϵ_A) dissolved in B(ϵ_B) (Eq. 1).

$$\epsilon_{\text{eff}} = \epsilon_B \frac{(1+2f)\epsilon_A + 2(1-f)\epsilon_B}{(1-f)\epsilon_A + (2+f)\epsilon_B} \quad (1), \text{ where } f \text{ is the fraction of small particles A}$$

embedded in medium B.

This theory however does not predict a percolation threshold for higher values of f and does not treat the media A and B symmetrically.

Walsh and Howie [6] improved on the early work of Fujimoto and Komaki [7] to develop an excitation theory based on electron trajectories, which accounts also for the excitation of interface plasmon modes at the embedded cluster-embedding medium interface (Eq. 2).

$$\begin{aligned} \text{Im}\left(-\frac{1}{\epsilon_{\text{eff}}}\right) = f \left\{ \text{Im}\left(-\frac{1}{\epsilon_A}\right) + g_{\text{int}} \left[\text{Im}\left(-\frac{3}{\epsilon_A + 2\epsilon_B}\right) - \text{Im}\left(-\frac{1}{\epsilon_A}\right) \right] \right\} + \\ + (1-f) \left\{ \text{Im}\left(-\frac{1}{\epsilon_b}\right) + g_{\text{ext}} \left[\text{Im}\left(-\frac{3}{\epsilon_A + 2\epsilon_B}\right) - \text{Im}\left(-\frac{1}{\epsilon_B}\right) \right] \right\} \end{aligned} \quad (2).$$

Equation 2 is written in terms of the two bulk loss functions $\text{Im}(-1/\epsilon_A)$ and $\text{Im}(-1/\epsilon_B)$ and the interface loss function $\text{Im}(-3/(\epsilon_A + 2\epsilon_B))$, with g_{int} and g_{ext} accounting for the interface contribution and the concomitant reduction in the bulk contribution (i.e. the interface contribution does not superimpose on the bulk contribution but replaces it with an appropriate factor that depends on the impact parameter). The factors g_{int} and g_{ext} can be expressed in terms of the filling fraction f , the particle diameter d , the velocity of the incident electron v and angular frequency ω of the excitation, for small spheres and filling fractions:

$$g_{\text{ext}} = (1 + 1/2f)^{-1} \quad ; \quad g_{\text{int}} = (1 + 3d\omega/v)^{-1} \quad (3).$$

For our experimental set-up, $g_{\text{int}} \approx 0.230 \cdot d[\text{nm}]$.

4 Results and Discussion

Figure 2 displays the bulk plasmon energy traces across the implanted layers, with the curves for the first three doses displaced upwards for visibility and comparison. The bulk plasmon energy does not show changes associated with Co until the last two doses (5 and $7 \times 10^{16} \text{ Co}^+/\text{cm}^2$), where there is, in the region closest to the field emitting surface, a 0.25 and 0.2meV decrease in the plasmon energy respectively, due to the increased weighting of the Co

dielectric function, with a bulk plasmon at 20.9eV, both through the filling fraction and the particle diameter. We also note that the highest dose sample has a further plasmon energy fluctuation of $\sim 0.3\text{eV}$ at the bottom of the implanted layer. Figure 3 shows the simulated change in the bulk plasmon energy as a function of the filling fraction (Equations 2 and 3), for the average diameters measured in Figure 1. The slightly larger diameter of Co clusters for the highest dose sample can be responsible for the slightly lesser decrease ($\sim 200\text{meV}$) in the bulk plasmon energy for the highest dose sample, as the interface plasmons contribute less to the overall spectra. This indicates that the

Figure 3. The simulated change in the bulk plasmon energy of Co clusters of two diameters embedded in SiO_2 , as a function of the filling fraction.

highest dose sample does not have a uniform Co implantation layer, but rather two regions appear to form at the top and the bottom of the implantation layer, with a relatively depleted layer in the middle; this could account for the slight reduction in the good field emitting properties of the highest dose sample and not going over the percolation threshold.

5 Conclusion

Valence electron energy loss spectroscopy is able to provide information about the structure and electronic properties of Co-implanted SiO_2 layers for field emission applications. We find that the bulk plasmon energy changes as the implantation dose changes, correlated with both the filling fraction and the cluster diameter. We observed a non-uniform implantation region appearing for the highest implantation dose, which could explain the slight increase in its field emission threshold.

References

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