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ORIGINAL RESEARCH

Investigation of coupled cobalt–silver nanoparticle system by plan view TEM

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Abstract We present a transmission electron microscopy (TEM) investigation of a coupled cobalt and silver nanoparticle system. A plan view *in situ* lift-out method for preparing samples for TEM using the focused ion beam (FIB) microscope was used. This technique is used to prepare high quality TEM samples with site specificity in a short time and with a high success rate. We demonstrate the ability of the plan view sample preparation technique to provide information about an ordered system of nanoparticles which could not be observed using standard FIB cross sectioning of the sample. High resolution TEM and energy dispersive X-ray spectroscopy mapping of both cross sectional and plan view samples are presented, clearly showing the significant benefit of plan view TEM analysis for certain samples.

1. Introduction

High resolution imaging and analysis are required for a broad range of materials and devices. As the development of semiconductor devices with ever smaller features [1], and the study of nanomaterials become more common, the need for high resolution imaging and analysis is more prevalent than ever [2–4]. The transmission electron microscope (TEM) can be used to provide a wealth of information about the structure and composition of materials at the atomic scale [5,6]. One requirement of TEM analysis is that the samples must be sufficiently thin, typically around 100 nm [7]. Conventional TEM sample preparation is achieved by a series of time consuming steps involving grinding, dimpling and ion milling of samples in order to thin them sufficiently [8]. A more

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efficient method of TEM sample preparation is achieved by the gallium focused ion beam (FIB).

The FIB can extract thin sections of material from bulk samples. Modern FIBs have both an ion beam for selective removal of material by milling, and an electron beam which provides high resolution imaging and charge compensation [9]. Regions of interest on the bulk sample can be located with the electron beam before being cross sectioned by the ion beam, allowing site-specific TEM analysis of samples. An *ex situ* lift-out method was initially employed in FIB sample preparation [10]. In this technique a lamella of material is cut free from the sample with the FIB. The sample is then placed under an optical microscope. The electrostatic attraction between a glass rod and the lamella is used to transfer the lamella to a TEM grid. This method had inherent limitations such as the inability to re-thin samples after lift out, it also had a relatively high failure rate (50–90% success yield) when compared with more recent techniques [11].

The FIB *in situ* lift-out technique, whereby the TEM lamella is removed from the sample and transferred to a TEM grid within the FIB chamber, has reduced the time and failure rates (90–100% success yield) traditionally associated with conventional TEM sample preparation. However, this cross sectioning technique can only provide a limited view of the sample. When analysing features which reside on or near the surface, a plan view of the sample would prove far more useful. Many previous attempts to prepare plan view TEM samples have involved polishing and chemical etching [12] or *ex situ* FIB lift-out [13]. We propose the use of the plan view *in situ* lift-out [14], this technique provides greater surface sampling and a view direction which cannot be achieved by typical cross sectioning.

In this article the plan view FIB *in situ* lift-out technique has been successfully demonstrated on a system consisting of Ag and Co nanoparticle arrays previously deposited on an optically transparent substrate. Bimetallic nanoparticle systems are currently under intense research in a range of fields due to their unique properties [15]. Such a system is of extraordinary interest as it supports localised plasmon resonances, *i.e.* oscillations of the free carrier within the nanoparticles [16]. As the system is also ferromagnetic, coupling between the magnetic and plasmonic properties of the nanocomposite layer can also be realized. The advanced functionalities have been previously demonstrated to produce novel interesting phenomena, such as plasmon enhanced magneto-optic activity [17,18]. Such a system is of potential interest for modulated sensing, imaging of magnetic fields and miniaturised magneto-optical devices and for enhanced spectroscopy due to the presence of "hot spots" in the interstitial space between the nanoparticles [19]. The work reported in this paper was used to locate and identify each individual nanoparticle within the prepared region. From this information the distribution and proximity of the two deposited materials was identified, giving a greatly enhanced understanding of the system.

2. Experimental

The sample investigated was produced using a novel self-assembly procedure named ATLAS (Atomic Terrace Low Angle Shadowing). In this method material is deposited using an e-beam evaporator in ultra-high vacuum (base pressure of 5×10^{-7} Pa) at a glancing angle onto a stepped substrate [20]. The stepped substrate was produced by annealing single crystal Al_2O_3 (0001) with a 6° miscut in the $[1\ \bar{2}\ 1\ 0]$ direction as previously described [21]. The sample was then loaded in the deposition chamber and inclined at 6° with respect to the flux of evaporated material. Co was deposited at normal incidence at a rate of 0.15 nm/minute for a nominal thickness of 1 nm. Subsequently, Ag was deposited at 11° using the same rate and nominal thickness. The result of the process consisted of nanoparticle arrays of both Co and Ag, deposited in an ordered fashion as shown in Fig. 1. This image has been taken using a Carl Zeiss Ultra Plus scanning electron microscope (SEM). However, the SEM utilised cannot establish where each material was exactly placed due to the small dimensions of the structures produced. TEM analysis was rendered necessary to establish where the Co and Ag were placed and how they interact due to their close proximity.

In order to protect the sample surface before FIB milling a thin gold coating would usually be sputtered onto the surface of the sample. However, the similar atomic mass of the gold coating and the deposited silver would lead to poor image contrast. Instead the surface was protected by coating the sample with a 75 nm layer of carbon using a Cressington 108 carbon/A carbon coater. A 5 nm layer of gold was finally deposited in a Cressington 108 auto sputter coater.

The FIBs used in these experiments were an FEI Strata 235 and a Carl Zeiss Auriga. In the Strata FIB the ion beam axis is orientated 52° relative to the electron beam, in the Auriga FIB the angle between the beams is 54°. In both microscopes a working distance of 5 mm was used. The Auriga FIB is equipped with a Kleindeik Nanotechnik micromanipulator needle and a Picoprobe GIS system for the lift-out procedure. The Auriga FIB can also mill with an ion beam energy as low as 2 keV which, when used as a final milling step, provides high quality samples with a damage layer as thin as 2–3 nm [22].

The TEM used for high resolution analysis was an FEI Titan 80–300 (S)TEM operating at an accelerating voltage of 300 kV.

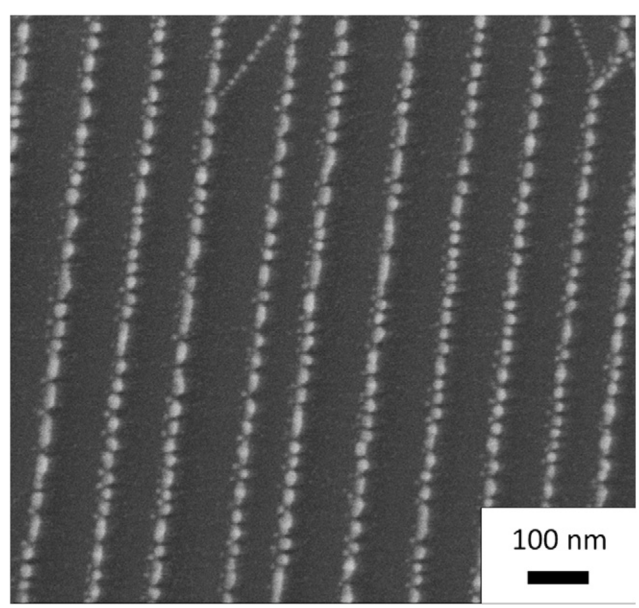

Fig. 1 SEM image of the cobalt and silver nanoparticles deposited on a stepped sapphire substrate.