Available online at www.sciencedirect.com
ScienceDirect
Thin Solid Films 516 (2008) 2082–2086
thin solid films
www.elsevier.com/locate/tsf

Structural and magnetic properties of self-assembled nickel nanoparticles in a yttria stabilized zirconia matrix

J.T. Abiade [a,*], G.X. Miao [b], A. Gupta [b], A.A. Gapud [c], D. Kumar [a,d]

[a] Department of Mechanical & Chemical Engineering, North Carolina A&T State University, 1601 E. Market Street, Greensboro, NC 27411, USA
[b] Depts of Chemistry & Chemical Engineering & Center for Materials for Information Technology (MINT), University of Alabama, Room 203 Bevill Building, Tuscaloosa, AL 35487, USA
[c] Department of Physics, University of South Alabama, ILB 103, Mobile, AL 36688, USA
[d] Condensed Matter Sciences Division, Oak Ridge National Laboratory (ORNL), Oak Ridge, TN 37831, USA

Received 19 March 2007; received in revised form 4 October 2007; accepted 22 October 2007
Available online 26 November 2007

Abstract

By controlling the early stages of thin film growth during laser ablation (i.e. Volmer–Weber type growth), we have synthesized magnetic nanocomposites consisting of nickel (Ni) nanoparticulates in multiple layers of yttria stabilized zirconia. The magnetic properties are a strong function of the nickel particle size, showing a clear transition from superparamagnetic to ferromagnetic characteristics. The coercivity at 300 K varies from 0 to nearly 4 A m^{-1} (~300 Oe) as the laser ablation time is increased. By applying the Scherrer formula to X-ray diffraction patterns, we estimated the average size of the Ni nanoclusters to be <5 – 20 nm for the four samples. For the superparamagnetic sample, a blocking temperature of ~100 K has been estimated by applying a field much lower than the saturation field and measuring magnetization versus temperature in field cooled and zero field cooled modes.

Keywords: Nanomagnetism; Self-assembly; Nickel; YSZ; Pulsed laser deposition (PLD)

1. Introduction

The controllable synthesis of nanostructured materials is a major challenge to full realization of next generation nanomagnetic devices. Self-assembly based techniques have generated widespread interest because of the potential to tailor the magnetic particle size, shape, and composition at the nanoscale [1]. Recently, physical vapor deposition (PVD) techniques have been used to grow self-assembled nanoclusters [2–7] in different thin film matrices for a variety of applications. Using PVD techniques, self-assembly is enabled by the tendency of metallic materials to grow as three-dimensional clusters or islands (Volmer–Weber growth) [8] before coalescing to form a continuous film. For sufficiently controlled growth processes, the nanocluster's size can be tailored, providing an alternate device fabrication route. PVD-based self-assembly techniques provide the opportunity for simultaneous synthesis, de-agglomeration, and passivation of nanomaterials *in-situ*. In this article, we report on the magnetic properties of multiple layers of nickel (Ni) nanoparticles embedded in yttria stabilized zirconia (YSZ, Y_2O_3–Zr_2O_3) thin films. YSZ is a well known material because of its chemical stability, dielectric characteristics, high coefficient of thermal expansion, and crystal structural and lattice constant similar to that of silicon. YSZ thin films are being explored for a variety of applications; as buffer layers for superconducting films on flexible metal tapes [9], as alternative high-dielectric constant materials on silicon substrates [10], and as electrodes in solid oxide fuel cells [11,12]. The chemical stability of YSZ allows *in-situ* passivation and de-agglomeration of the embedded nickel nanoparticles and the compatibility of YSZ with Si facilitates Si-based magnetic devices. Furthermore, YSZ may be grown epitaxially on Si under the appropriate deposition conditions. The present

* Corresponding author. 127 Holden Hall, MC 0237, Blacksburg, VA 24061, USA. Tel.: +1 540 231 1469; fax: +1 540 231 8919.
E-mail address: jabiade@vt.edu (J.T. Abiade).

0040-6090/$ - see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.tsf.2007.10.103

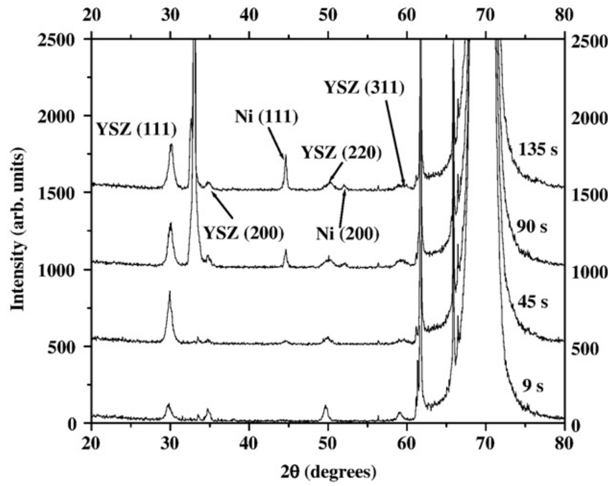

Fig. 1. XRD patterns (θ–2θ scans) for the samples deposited at different Ni deposition times. Substrate peaks have been labeled with an asterisk (*).

study attempts to understand the influence of the Ni ablation time on the growth, morphology, and magnetic properties of self-assembled Ni nanoclusters in a YSZ thin film matrix.

2. Experimental details

Nickel nanoparticulates were embedded in polycrystalline YSZ thin films on Si (100) substrates by laser ablation of Ni and YSZ targets during pulsed laser deposition (PLD). The PLD system consists of a multi-target carousel and a KrF excimer laser with $\lambda = 248$ nm (Lambda Physik). Prior to each deposition, the silicon substrates were cleaned in acetone and etched in dilute hydrofluoric acid to remove the native oxide layer. After the desired chamber pressure was reached ($\sim 1.3 \times 10^{-8}$ Pa), the substrates were maintained at the deposition temperature (650 °C) for 30 min prior to each run. To avoid formation of NiO, which is antiferromagnetic or Ni/NiO core/shell structures, oxygen was not used during the depositions. All films were deposited in vacuum. The target to substrate distance was maintained at 5.9 cm. The multi-layered structure consisted of an initial YSZ layer ($\sim$50 nm) and alternating layers of nickel nanoparticles and YSZ spacer layers ($\sim$25 nm). Each sample consists of 5 alternating Ni/YSZ layers. The Ni particulate size was altered by varying the number of laser pulses, or deposition time, at a laser frequency of 10 Hz.

X-ray diffraction (XRD) analysis was performed using a four-circle diffractometer with a copper source ($\lambda = 0.154$ nm) manufactured by Bruker-AXS (D8 Discover model). The magnetic properties of the Ni–YSZ nanocomposites were studied using a physical property measurement system equipped with the vibrating sample magnetometer (VSM) option from Quantum Design. The VSM was used to study the field and temperature dependence of the magnetic moment of multiple layers of Ni particulates in an insulating YSZ matrix. For magnetization versus temperature measurements, the moment was measured in both the zero field cooled (ZFC) and field cooled (FC) modes. During the ZFC measurement, the samples were cooled to 10 K with no applied field. The moment was then measured while warming the samples up to 300 K in the presence of a magnetic field. For FC measurements, the samples were cooled to 10 K in the respective field and the moment was measured while warming to room temperature. The temperature dependence of the coercivity and remanence ratio was obtained from the various magnetization versus field loops measured at different temperatures. Magnetic property values are expressed in SI units.

3. Results and discussion

Fig. 1 shows the XRD data for the Ni–YSZ samples with different Ni deposition times. The patterns have been vertically shifted for clarity. The YSZ matrix is polycrystalline in all samples with a face centered cubic (FCC) structure similar to that of the underlying Si substrate. In addition to the Si (400) substrate peak at $\sim$69°, (111), (200), (220), and (311) peaks from the YSZ films are present. Extraneous peaks that can be assigned to Cu Kβ (62° and 67°) and tungsten (65°) radiation are also present in the patterns. The Ni (111) peak ($\sim$44°) is visible in all of the patterns except the sample with Ni deposition time of 9 s. Magnetic measurements (discussed later), confirm the presence of Ni in this sample. The Ni (200) peak is also visible in the samples with Ni deposition times of 90 and 135 s. Using the Scherrer equation ($0.9\lambda/B\cos(\theta)$); we estimate the average Ni particle size ranges from <5 to $\sim$20 nm. Also in Fig. 1, the intensity of the Ni (111) peak is enhanced as the Ni ablation time is increased, which indicates an increase in the average Ni particle size with increasing deposition time.

Fig. 2 shows the magnetization versus magnetic field (*M–H*) loops at 300 K for the samples with various nickel deposition times. The 300 K hysteresis loop for the sample with 9 s deposition time is shown in the inset of Fig. 2. The *M–H* loops in Fig. 2a clearly demonstrate classical magnetic size effects in which the samples undergo superparamagnetic (SPM) to ferromagnetic (FM) transition as the nanoparticle size is increased. The coercivity values obtained from each curve are: 0, 0.13, 1.8 and 2.0 A m^{-1} for deposition times of 9, 45, 90, and 135 s, respectively. A clear magnetic signal, from the Ni

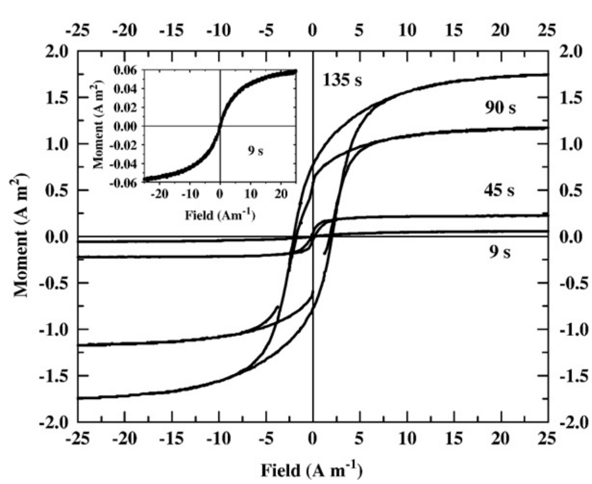

Fig. 2. *M–H* loops recorded at 300 K for samples deposited at different Ni deposition times. Inset graph presents data for the sample deposited for 9 s.