Emerging Materials
Room On Demand - Session EM8
Nanolaminates

EM8-1 Properties of Atomic Layer Deposited ZrO_2 or Fe_2O_3 Based Multilayers, ***Helina Seemen**, K. Kukli, A. Tamm,* University of Tartu, Estonia

Research devoted to the achievement of multiferroic thin-film materials is actual, and the task itself has appeared to be quite challenging. At the same time, it could also be rewarding in the case of success due to prospective applications as these materials are useful for non-volatile memories and electromagnetic sensor materials. In this study, five-layer nanolaminates consisting of alternately deposited ZrO_2 and Co_3O_4 layers, and two-layer structures consisting of Fe_2O_3 film and BiOCl nanoflakes were deposited to explore their potential advanced magnetic properties [1, 2]. The main goal was to achieve a ferromagnetic-like response with the measurable coercivity values getting as high as ten kOe. The Fe_2O_3-BiOCl combination was partly selected due to the possible formation of bismuth ferrite, which is known to be one of the most promising multiferroic materials, at the interfaces.

The ZrO_2-Co_3O_4 5-layer nanolaminates were grown by atomic layer deposition at 300 °C from $ZrCl_4$ and $Co(acac)_3$ as metal precursors and O_3 as the oxygen precursor. The Fe_2O_3-BiOCl two-layer thin-film structures were deposited from $FeCl_3$, $BiCl_3$ and H_2O at 375 °C.

The results showed that the multilayers of both studies were crystallized in the as-deposited state. In the ZrO_2-Co_3O_4 5-layer nanolaminates, the cubic and monoclinic ZrO_2 phases and cubic Co_3O_4 phase were present. Orthorhombic ε-Fe_2O_3 and tetragonal BiOCl phases were detected in the case of Fe_2O_3-BiOCl two-layer thin-film structures. In Table I, selected multilayer structures, their total thicknesses and measured coercivity values are presented. Magnetic hysteresis loops showed nonlinear and saturative magnetization and measurable coercivity, indicating ferromagnetic-like behaviour at room temperature. The highest coercivity value measured was 9757 Oe (776.4 kA/m), which characterized one particular Fe_2O_3-BiOCl two-layer thin-film structure (Table I). SEM images of this type of multilayer structure are displayed in Figure 1. In the case of the ZrO_2-Co_3O_4 nanolaminates, the coercivity values were 21 and 32 Oe (1.7 to 2.5 kA/m) (Table I). All five layers of the nanolaminates were clearly distinguishable (Figure 2).

[1] H. Seemen, K. Kukli, T. Jõgiaas, P. Ritslaid, J. Link, R. Stern, S. Dueñas, H. Castán, A. Tamm, Properties of atomic layer deposited iron oxide and bismuth oxide chloride structures, J. Alloys Compd., 846 (2020) 156099.

[2] H. Seemen, M. Rähn, K. Kalam, T. Sajavaara, S. Duenas, H. Castan, J. Link, R. Stern, K. Kukli, A. Tamm, Properties of atomic layer deposited nanolaminates of zirconium and cobalt oxides, ECS J. Solid State Sci. Technol., 7 (2018) P402-P409.

EM8-2 Evaluation of the Near-Zero Temperature Coefficient of Resistivity (Nz-TCR) of ALD $TiSi_xN$ Films, ***Corbin Feit**, S. Berriel ,* University of Central Florida*; A. Dhamdhere, B. Nie, H. Cho, H. Kim, S. Chugh, S. Rathi, N. Mukherjee,* Eugenus, Inc.*; P. Banerjee,* University of Central Florida

Atomic Layer Deposition (ALD) of ternary $TiSi_xN$ leads to nanocomposites of metallic TiN atomically mixed with insulating Si_3N_4. Formulating $TiSi_xN$ films with various Ti:Si ratios lead to the emergence of a temperature regime where resistivity is independent of thermal drift, denoted as near-zero temperature coefficient of resistivity (nz-TCR). Further, the ease with which nanocomposites of $TiSi_xN$ can be deposited using ALD offer precise tunability in Ti:Si ratio, thickness, mass density, crystallinity and electrical properties.

Recently, our group explored $TiSi_xN$ films deposited using a Eugenus® 300 mm commercial QXP mini-batch system by modulating the ratio of Ti and Si precursors with NH_3 as a co-reactant.Si-content was varied from 0 at % (pure TiN) to 24.2 at % Si while maintaining thickness ~ 140 nm. The X-ray reflectivity and grazing incidence X-ray diffraction measurements showed a reduction in film density and transition from nano-crystalline to pure amorphous phase with increase in Si-fraction. Spectroscopic ellipsometry revealed the optical constants, composition, and electrical resistivities and were supported by X-ray photoelectron spectroscopy and electrical measurements. Room-temperature resistivity measurements show an increase in film resistivity with increasing at % Si. Temperature-dependent Van der Pauw measurements found a nz-TCR of -23 ppm K^{-1} in the temperature range of 298 K – 398 K and at 3.4 at % Si content.

We have now discovered that an at % Si = 3.0% induces a nz-TCR of -5.7 ppm K^{-1} from 80 K – 420 K – one of the best reported nz-TCR values for ALD thin films. Fine tuning the at % Si in $TiSi_xN$ films, possible only via ALD, significantly elongated the temperature window of nz-TCR behavior. Mapping the local conductivity of individual grains through conductive atomic force microscopy (c-AFM) indicated higher resistance at the grain boundaries. The local composition at the grain boundaries may play a major role in determining the nz-TCR behavior of $TiSi_xN$ films. In addition, variable temperature Hall effect measurements were performed to provide deeper insights into the nz-TCR mechanism, decoupling carrier concentration from carrier mobility effects while determining film resistivity.

Compared to other nz-TCR films, which are deposited using physical vapor deposition techniques, ALD based nz-TCR films presents a unique synthesis platform for interconnect technology in topologically complex, 3D devices, circuits and sensors that undergo large temperature variation during operation but need to maintain stability in their electrical characteristics.

Author Index

Bold page numbers indicate presenter