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Citation: CARUANA, A.J. ...et al., 2016. Demonstration of polycrystalline thin film coatings on glass for spin Seebeck energy harvesting. Physica Status Solidi: Rapid Research Letters, 10 (8), pp. 613-617.

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Metadata Record: https://dspace.lboro.ac.uk/2134/22004

Version: Published

Publisher: © The Authors. Published by Wiley

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Demonstration of polycrystalline thin film coatings on glass for spin Seebeck energy harvesting

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Received 18 April 2016, revised 12 June 2016, accepted 24 June 2016
Published online 30 June 2016

Keywords magnetic materials, thermoelectrics, thin films

The spin Seebeck effect, a newly discovered phenomena, has been suggested as a potential ‘game changer’ for thermoelectric technology due to the possibility of separating the electric and thermal conductivities. This is due to a completely different device architecture where, instead of an arrangement of p- and n-type pillars between two ceramic blocks, a thermopile could be deposited directly onto a magnetic film of interest. Here we report on the spin Seebeck effect in polycrystalline Fe₃O₄:Pt bilayers deposited onto amorphous glass substrates with a view for economically viable energy harvesting. Crucially, these films exhibit large coercive fields (197 Oe) and retain 75% of saturation magnetisation, in conjunction with energy conversion comparable to epitaxially grown films. This demonstrates the potential of this technology for widespread application in harvesting waste heat for electricity.

1 Introduction A new direction in thermoelectric research has recently emerged where it could be possible to separate the electric and thermal conductivities in a device: the parameters typically limiting conventional thermoelectric generators [1]. This is due to the discovery of the spin Seebeck effect (SSE), whereby a spin polarised current is generated in response to a thermal gradient in a magnetised material [2]. By adding a thin layer of a heavy metal such as Pt, this spin polarised current can be converted to a charge current (i.e. conversion of heat into electricity across two separate layers). Such spin Seebeck based devices enable a completely different device architecture where, instead of an arrangement of p- and n-type pillars between two ceramic blocks, a thermopile could be deposited directly onto a magnetic film of interest [3]. Up until now, the focus of SSE measurements has been on epitaxial growth. Here we demonstrate comparable power conversion in polycrystalline Fe₃O₄:Pt bilayers deposited onto amorphous glass substrates, with respect to epitaxially grown Fe₃O₄ [4]. This is a critical step towards demonstrating the potential for widespread application of this material in harvesting waste heat for electricity.

Conversion of the spin current generated by the SSE into a useful voltage is achieved by placing a heavy paramagnetic metal such as Pt (the ‘PM’ layer) in direct contact with the magnetic material of interest (the ‘M’ layer). When a spin current is injected into the PM layer an electric potential, $E_{\text{SSE}}$, is generated by the spin orbit interaction: the inverse spin Hall effect (ISHE) [5]. This is the primary mechanism for observation of the SSE and whilst there have now been several reports of this effect, the most commonly studied materials are yttrium iron garnet (YIG) as the ‘M’ layer (due to its favourable magnon and highly resistive insulating properties [1]), and Pt as the ‘PM’ layer (due to reliable spin conversion [1–3, 5]).

There are two measurement configurations for the SSE: the longitudinal SSE, where a thermal gradient is applied perpendicular to the M:PM interface (Fig. 1(a)); and...
the transverse SSE, where a thermal gradient is applied parallel to the M:PM interface (Fig. 1(b)). In both cases the M layer is magnetised in plane, with a spin current generated perpendicular to it. Whilst initial experiments employed the use of the transverse configuration [2], the longitudinal configuration lends itself more readily to waste heat harvesting [1] and is the geometry studied here.

The key difference between conventional Seebeck energy harvesting devices (Fig. 1(c)) and a spin Seebeck based energy harvesting device (Fig. 1(d)) is the material(s) in which thermal and charge conversion occurs. In a conventional Seebeck based device thermal currents ($J_\theta$), are converted directly to charge currents, ($J_\sigma$), by the Seebeck effect in the active material(s) and the efficiency of such a device is dependent on the thermal ($\kappa$) and electric ($\sigma$) conductivities as well as the Seebeck coefficient ($S$) of the active material. In a spin Seebeck based device the thermal current is converted to a spin current ($J_\sigma$) in the M layer, and then later converted to a charge current in the PM layer; thus the parameters that control efficiency ($\kappa$, $\sigma$) are now in two distinctly separate layers. The main advantage of spin Seebeck based energy harvesters is not only that $\kappa$ and $\sigma$ can be altered independently through careful choice of the M and PM layers, but also that the voltage generation, $V_{\text{SSE}}$, will scale linearly with separation of the voltage contacts ($\Delta$).

So far, the main focus of this research area has been: (i) to identify different material systems that exhibit this effect (whether metallic [6], insulating [7], semiconducting [8], or oxides [9]); (ii) to try to understand the impact of substrate induced phonon drag [10]; or (iii) to rule out erroneous contributions such as proximity induced magnetism in the Pt layer [11], or the anomalous Nernst effect (ANE, an electric field generated in a conductive magnetised material subjected to a temperature gradient).

With respect to the impact of the substrate on the magnitude of the observed voltage, it was recently shown by Siegel et al. that whilst substrate induced phonon drag might play a role in transverse measurements [12, 13], this is not the case in the longitudinal configuration [14]. Where the M layer is highly resistive compared to the PM layer, as is the case here, the impact of the ANE is considered negligible [1, 4].

With regards to metrology of the SSE the temperature difference, $\Delta T$, is often measured across the entire device (i.e. substrate, M layer, and PM layer), and used alongside the measured voltage generation to quote a value for the spin Seebeck coefficient whereas it is the heat flux [15] at each interface that is likely the controlling factor. This will be particularly important when considering the efficiency of spin Seebeck based thermoelectrics.

2 Experimental details The samples tested here were part of a series of 80 nm thick Fe$_3$O$_4$, 1–13 nm thick Pt, deposited on glass. They were deposited in vacuum by pulsed laser deposition (PLD) onto $10 \times 10$ mm² and $22 \times 22$ mm² glass slides, which were baked out at 400 °C prior to the growth of the Fe$_3$O$_4$ layer. The Pt layer was then deposited in-situ at room temperature. The Fe$_3$O$_4$ and Pt layers were deposited from Fe$_3$O$_4$ (Pi-Kem purity 99.9%) and Pt (Testbourne purity 99.99%) targets using ablation fluences of 1.9 ± 0.1 and 3.7 ± 0.2 J/cm², respectively. Fe$_3$O$_4$ was chosen due to its large spin polarization ($\sim 80\%$ [16]), low thermal conductivity (at 300 K: $\kappa_{\text{film}} \sim 2–3.5$ W/m/K [17], $\kappa_{\text{bulk}} \sim 2–7$ W/m/K [18]), and relative abundance of the constituent elements. In this respect it is comparable to YIG, with the advantage of the more abundant constituents.

X-ray diffraction (XRD) was obtained using a Bruker D2 Phaser. X-ray reflectivity (XRR) was used to determine the film thickness(es). Example XRR and XRD data is given in the Supporting Information. Of particular note is the following: XRR data indicated a typical Fe$_3$O$_4$ film thickness of $t = 78 \pm 2$ nm, and a roughness of $1.5 \pm 0.2$ nm.

Cross sections of a representative sample from the series studied here (SSE5a: 0.3 mm glass, 79 nm Fe$_3$O$_4$, 2.5 nm Pt), were prepared for transmission electron microscopy (TEM) analysis using the in-situ lift-out approach. A dual-beam instrument (FEI Nova Nanolab 600) fitted with an Omniprobe™ micromanipulator was used. To preserve and mark the original surface of the PM Pt thin film, a $\sim 50$ nm Au coating was evaporated on the sample surface ex-situ by physical vapour deposition, and a further Pt layer $\sim 1$ µm was laid in the FIB prior to the standard routine for TEM specimen lift-out.

Microstructural characterisation of the cross-sections and composition line-scans across the thin film layers were performed using a FEI Tecnai F20 G2 S-Twin field emission gun (FEG) TEM. The TEM was operated at 200 kV and equipped with an Oxford Instruments X-Max 80 mm² TLE detector for energy dispersive X-ray (EDX) spectroscopy.
Magnetisation as a function of applied magnetic field was measured using a quantum design magnetic properties measurement system (SQUID).

Room temperature sheet resistance was obtained using the Van der Pauw method with a Keithley 6221/2182 nanovoltmeter and current source in conjunction with a Keithley 705 scanner. Spin Seebeck measurements were obtained in the longitudinal configuration, where $\Delta T$ was monitored by type E thermocouples and a Peltier cell provided the heat source. The contact separation was fixed at 5.6 ± 0.4 mm.

Further information, including a full list of samples and additional characterisation can be found in the Supporting Information.

3 Results and discussion

Figure 2 presents TEM and EDX analysis of SSE5a (0.3 mm glass, 79 nm Fe$_3$O$_4$, 2.5 nm Pt), which is used to illustrate the typical microstructure. Figure 2(a) and (b) show scanning TEM bright field (STEM/BF) and high angle annular dark-field (HAADF) images of the sample. The grain boundaries of columnar Fe$_3$O$_4$ seen in the STEM/BF image (Fig. 2(a)) that are not visible in the STEM/HAADF image of (Fig. 2(b)), indicates that the Fe$_3$O$_4$ grains are all the same phase. A thin continuous paramagnetic Pt layer is clearly seen running on top of the Fe$_3$O$_4$ layer following the wavy surface of the Fe$_3$O$_4$ layer. This is followed by a layer of grease (residual from the spin Seebeck measurements), Au and FIB Pt.

Figure 2(c) shows a conventional high resolution TEM (HRTEM) micrograph of the PM Pt layer recorded at the very edge of the FIB lamella where the section was the thinnest (~100 nm). It indicates 2–3 nm thick crystallized Pt stacking on top of the Fe$_3$O$_4$(111) planes. The two grains have an orientation relationship of $[011]_{\text{Pt}} || [011]_{\text{Fe}_3\text{O}_4}$, $[111]_{\text{Pt}} || (111)_{\text{Fe}_3\text{O}_4}$, which minimises the interface energy due to minimal lattice mismatch of $d(111)_{\text{Pt}}$ (0.226 nm; JCPDS card 4-802) and $d(222)_{\text{Fe}_3\text{O}_4}$ (0.242 nm; JCPDS card 19-629). Further chemical composition linescan profiles perpendicular to the interfaces of the layers are shown in Fig. 2(d).

The voltage generated, $V_{\text{SHE}}$, was measured as a function of applied magnetic field, $B$ (where $B = \pm 800$ Oe), and temperature difference, $\Delta T$, across the devices (substrate + M layer + PM layer). For simplicity, and to enable a comparison of our data to other work we define the parameter $S_{\text{SSE}}$, which refers to the voltage generation per unit length and Kelvin of temperature difference across the device:

$$S_{\text{SSE}} = \frac{V_{\text{SHE}}}{s \Delta T},$$

where $s$ is the contact separation defined in Fig. 1(a), $V_{\text{SHE}}$ is the voltage measured, and $\Delta T$ is the temperature difference across the device.

Figure 3 summarises the magnetic, electric and thermoelectric measurements of the series of SSE devices where the field dependence of $S_{\text{SSE}}$ is shown for SSE5a alongside the corresponding $M$–$H$ curve for that sample (Fig. 3(a)). Magnetometry at room temperature exhibited a coercive field, $H_c = 197 \pm 5$ Oe, saturation magnetisation, $M_s = 90$ Am$^2$/kg, and a remanent moment of $M_r = 68$ Am$^2$/kg. The spin Seebeck measurements (Fig. 3(a) and (c)) showed the expected magnetic field dependence (both the ANE and SSE would depend on the magnetisation of the M layer) and $I_{\text{PM}}$ dependence (thicker Pt would ‘short’ the effect of proximity induced magnetism in the Pt layer, as would the decreasing resistivity associated with thicker layers exhibited in Fig. 3(b)).

To rule out the contribution of the ANE and proximity effect to the total signal, additional control samples were measured and are discussed in detail in the Supporting Information. For completeness, indicative values for control sample 1 (Fe$_3$O$_4$ : Au), and control sample 2 (80 nm Fe$_3$O$_4$: 5.1 nm Au: 1.1 nm Pt) are shown in Fig. 3(c). Overall the control data suggested that the dominant contribution to the observed voltage was due to the SSE, which is consistent with the observation made by Ramos et al. [4].

The relationship between $I_{\text{PM}}$ and the measured $S_{\text{SSE}}$ has also been simulated following the arguments presented by Weiler et al. [21], and summarised in Eq. (2):

$$S_{\text{SSE}}(I_{\text{PM}}) \propto \frac{g_s \theta_{\text{SH}} \gamma_{\text{SD}} \rho_{\text{PM}} \tanh \left( \frac{I_{\text{PM}}}{2 \lambda_{\text{SD}}} \right) \left( \frac{T}{B} \right)^{\frac{3}{2}}}{I_{\text{PM}} M_s \left[ h + 2 g_s \rho_{\text{PM}} \gamma_{\text{SD}} e^\gamma \coth \left( \frac{I_{\text{PM}}}{\gamma_{\text{SD}}} \right) \right] \left( \frac{T}{B} \right)^{\frac{3}{2}}},$$

where $h$, $g_s$, $\rho_{\text{PM}}$, $\gamma_{\text{SD}}$, $\lambda_{\text{SD}}$, $\theta_{\text{SH}}$, and $\gamma$ are constants.

To illustrate the typical microstructure and additional characterisation, Fig. 2(b) shows scanning TEM bright field (STEM/BF) and high angle annular dark-field (HAADF) images of the thin film, respectively. (c) Conventional HREM of the PM Pt layer. (d) EDX line-scan performed perpendicular to the interfaces of the layers.
where $l_{SD}$, $\rho_{PM}$, $\theta_{SH}$ are the spin diffusion length, thickness, resistivity, and spin Hall angle of the PM layer, respectively; $D$ and $M_i$ are the spin wave stiffness coefficient and saturation magnetisation of the M layer; $g_i$ is the spin mixing conductance at the interface, as defined by Qiu et al. [22] and $h$ and $e$ are Planck’s constant and the charge of an electron.

Intrinsic material parameters such as $l_{SD}$, $\theta_{SH}$, $D$ and $M_i$ would not be expected to vary too much between samples in this study, leaving the resistivity of the PM layer ($\rho_{PM}$), which was measured, as shown in Fig. 3(b), and $g_i$, which will be heavily dependent on the quality of the M:PM interface. Thus, $S_{SSE}$ was simulated for various values of $g_i$, where this relationship was found to agree well with the experimental data when $l_{SD} = 2$ nm, consistent with values reported for Pt at room temperature [21]. Whilst in general, an increase in $S_{SSE}$ with decreasing thickness is a result of the increasing resistivity of the PM layer, for $t_{PM} < 3$ nm the reproducibility of the measurements deteriorated (as might be expected from the sensitive impact of the interface condition on the measurement) [23]. It would be expected that the impact of producing polycrystalline films can lead to variations in the interface quality (with regards to spin conversion [22] and thermal resistance [24]) between samples and across the device surface (parameterised by $g_i$), as shown by the simulations in Fig. 3(c), and the error bars on the individual datapoints.

In order to identify the effectiveness of these films with regards to thermal conversion we draw comparison with the SSE measured for epitaxially grown Fe$_3$O$_4$ by Ramos et al. In their work they observed voltages of the order of 1.2 $\mu$V/K/m (50 nm Fe$_3$O$_4$ deposited onto 0.5 mm SrTiO$_3$ using PLD, with an 8 $\times$ 4 mm, 5 nm thick Pt layer [4]), which equates to $S_{SSE} = 150 \mu$V/K/m [4]. Initial comparison of these results with our work suggests a drop of a factor of 4.2 by depositing onto an amorphous substrate (for the same Pt thickness $S_{SSE} = 35.7 \mu$V/K/m for Fe$_3$O$_4$ on glass [this work]). However, as discussed earlier, to meaningfully compare measurements of the SSE across various different material systems the heat flux, or temperature difference across the active layer $-\Delta T_2$, and not an arbitrary temperature difference $\Delta T$ needs to be considered [15]. A good approximation of this can be obtained by considering the heat flux, $\Phi$, at each interface in a trilayer system under steady state conditions:

$$\Phi = \frac{q}{A} = \frac{\Delta T}{\kappa_1 + \frac{d_1}{\kappa_1} + \frac{d_2}{\kappa_2} + \frac{d_3}{\kappa_3}},$$

where $\{d_1, d_2, d_3\}$ and $\{\kappa_1, \kappa_2, \kappa_3\}$ are the thicknesses and thermal conductivities of the top layer (1), FM layer (2) and substrate (3), respectively; $\Delta T$ is the temperature difference across the entire device; and $A$ is the contact area at each interface, as defined in Fig. 3(d). For substrates with significantly different thermal conductivities ($\kappa_i$), $\Delta T_2$ and hence $\Phi$ could vary dramatically, as shown in Fig. 3(e). A comparison of our measurements of polycrystalline Fe$_3$O$_4$ with the study of epitaxially deposited Fe$_3$O$_4$ onto SrTiO$_3$ [4] is summarised in Table 1. Whilst the substrate, M, and PM layers have similar thicknesses, the heat flux, $q$, determined using Eq. (3) is an order of magnitude larger due to the significantly higher thermal conductivity of the substrate. This leads to the conclusion that whilst the measu-
ured voltage for Fe₃O₄ on glass was lower, this is likely due to a lower temperature gradient across the magnetic layer itself and not a pronounced drop in the energy conversion efficiency of the device. If we were to consider the spin Seebeck coefficient in terms of temperature difference across the M layer only (i.e. as a measure of the energy conversion), \( S_{\text{SE}} \):

\[
S'_{\text{SE}} = \frac{f_{\text{ISHE}}}{s \Delta T},
\]

this would translate to 0.60 V/K/m for this study compared to 0.58 V/K/m for Fe₃O₄ on SrTiO₃. To further demonstrate this, the impact of \( \kappa \) on the reported \( S_{\text{SE}} \) is also shown in Fig. 3(f).

### 4 Conclusion

We have demonstrated comparable energy conversion in polycrystalline Fe₃O₄ films deposited onto glass with respect to epitaxial films. This indicates viable low cost production of spin Seebeck based energy harvesting coatings provided a suitable alternative to Pt can be found. This will require investigation of alternative PM contacts that find a compromise between the parameters identified in Eq. (2), namely \( \Delta M_{\text{PM}}, \mu_{\text{PM}}, \) and \( \theta_{\text{Bil}} \). Furthermore, the large remanent moment and coercive field observed in these Fe₃O₄ films (\( M_r = 0.75 M_c, H_c = 197 \text{ Oe} \)), suggests the potential for stable voltage generation in spin Seebeck based devices of the order of 0.6 V/K/m that could be further improved by using a thermopile device structure.

### Supporting Information

Additional supporting information may be found in the online version of this article at the publisher’s website.

### Acknowledgements

This work was supported by EPSRC First Grant (EP/L024918/1). Supporting Information is available online from Wiley InterScience or from the corresponding author. Supporting data will be made available via the Loughborough data repository under DOI 10.17028/rd.lboro.2001258.

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