Published in final edited form as:
Proc IEEE Sens. 2016 ; 2016: . doi:10.1109/ICSENS.2016.7808845.

Optimization of Metglas 2605SA1 and PZT-5A Magnetoelectric Laminates for Magnetic Sensing Applications

Eugene Freeman[1], **Joshua Harper**[2], **Nishit Goel**[1], **Steven J. Schiff**[2], and **Srinivas Tadigadapa**[1]

[1]Department of Electrical Engineering, The Pennsylvania State University, University Park, Pennsylvania, USA

[2]Department of Engineering Sciences and Mechanics, The Pennsylvania State University, University Park, Pennsylvania, USA

Abstract

Via optimization of the mechanical coupling, alignment of Metglas® magnetic domains, relief of residual stress, and operation of the PZT-5A under a DC electric field of 2 kV/cm an unprecedented magnetoelectric voltage coefficient of 9.52 V/cm-Oe is achieved; resulting to a magnetic field sensitivity of 150 pT at 20 Hz for a d31 Metglas®/PZT-5A laminate. Mechanical coupling is improved by reducing the thickness and porosity of the epoxy. The Metglas® residual stress reduction and easy axis alignment is accomplished by a 30 minute 400 °C anneal under a 1600 Oe magnetic field in vacuum. Finally, a DC electric field bias is applied to increase the d_{31} coefficient of the PZT-5A piezoelectric.

Keywords

Magnetoelectric; Magnetometer; Metglas 2605SA1; Annealing; PZT

I. Introduction

The magnetoelectric (ME) coupling effect has been used extensively in the design of highly sensitive room temperature magnetic sensors [1]. The ME effect is realized by the use of laminate structures in which a magnetostrictive ribbon is bonded to a piezoelectric such that magnetically induced strain in the magnetostrictive layer produces a stress and subsequently charge in the piezoelectric layer. This effect can be characterized by the ME voltage coefficient, α_{ME}, which is given by:

$$\alpha_{ME} = \Delta V/(t \Delta H) \quad (1)$$

where ΔV is the measured electric potential in the piezoelectric, t is distance between electrodes across which the voltage on the piezoelectric is measured and H is the external magnetic field. For a maximal α_{ME}, a laminate must possess a high magnetostrictive (q_{33}) and piezoelectric (d_{33} or d_{31}) coefficients, and a high coupling coefficient between the layers. As a result, highly sensitive magnetometers utilize high q_{33} materials such as

Metglas® 2605SA1 (q_{33} =3.6 ppm/Oe) [2] and high piezoelectric coefficients materials such as PMN-PT (d_{33}=1800 pC/N) [3] and PZT-5A(d_{33}/d_{31}=374/−171 pC/N) [4].

Optimal material choice is critical to achieve a high α_{ME} coefficient; however aspects of the coupling coefficient have been shown to be at least as important in determining the overall sensitivity, such as bonding par α_{ME} ters between layers, geometric parameters for magnetic flux concentration, and in the case of Metglas foil, anneal time and temperature.

Optimization of bonding parameters has been studied experimentally and through various models. Liu et al. used finite element method to show that in a laminate composite with PZT sandwiched by two layers of Terfenol-D, thinner layers of epoxy with higher shear modulus significantly increase α_{ME} [5]. These results were consistent with Nan et al. who used Green's function technique to investigate the effect of bonding and further noted that any imperfection in the bonding layer could also reduce α_{ME} [6]. Filippov et al. showed that α_{ME} decreases with increasing epoxy bond layer thickness [7]. Similarly, increasing Young's modulus of the epoxy increases α_{ME} in the accompanying model.

Geometric parameters of the laminate structure have also been shown to affect α_{ME}. Fang et al. showed that higher flux concentration could be achieved by maximizing the length of the ribbon and minimizing the width of the magnetostrictive layer [8]. It has also been shown that the thickness ratio between piezoelectric and magnetostrictive layers has an effect on α_{ME} [9].

Annealing Metglas® foils has been shown to improve α_{ME} for ME laminates. In a study of Metglas® ribbons alone, Bucholtz et al. showed that annealing temperatures greater than 300 °C (but less than the crystallization temperature), while magnetically poled, improved magnetostriction [10]. Yang et al. studied the effect of heat treatment of Metglas® on the α_{ME} of Metglas®/PZT laminate composites [11]. Samples of Metglas® were annealed at 100 °C intervals between 150 – 650 °C (crystallization temperature of Metglas® 2605SA1 is 508 °C) for 1 hour. M-H loops showed that at 350 °C there was no loss in magnetic moment and there was no increase in hysteresis, however at 450 °C both negative effects were present. Various analysis methods revealed that minimal nucleation of partially crystalline structures were observed at 350 °C with minimal clustering and virtually no oxidation as compared with 400 °C anneals which show crystallization and a twofold increase in the oxidation layer. In the composite sensor, it was shown that an anneal temperature of 350 °C offered a 1.4x sensitivity increase over those annealed at 300 °C and 1.5x sensitivity increase over those annealed at 400 °C. These results imply that there is an anneal temperature and time which will maximize the improved magnetostriction and minimize the losses which come with crystallization.

The present study explores the consolidation of epoxy application, Metglas® annealing, and DC electric field biasing optimizations to achieve an optimized ME device. A mechanical clamping method during epoxy curing is utilized to realize thin and non-porous bonding layer resulting in increased sensitivity for Metglas®/PZT laminate composites. Furthermore, we use COMSOL to simulate the effects of changing the epoxy thickness and Young's Modulus. We optimize the Metglas® annealing condition by varying the temperature from

250 – 400 °C in air and vacuum with 1600 Oe magnetic poling. We further optimize the device by applying up to 2 kV/cm DC electric field poling to the PZT during the measurements.

II. Device Construction and testing

The ME laminates are made using 2 layers of 23 μm thick 30 × 5 mm Metglas® 2605SA1 ribbons epoxied above and below a 3 × 13 × 0.2 mm PZT-5A using EPO-TEK H20E, a conductive epoxy, as illustrated in Fig. 1. The structure is placed in a clamp (unless otherwise stated) and the epoxy is cured at 95 °C for at least 3 hours. The final structure is then epoxied on a custom ceramic holder with silver electrodes, which are epoxied (EPO-TEK H20E 3 hour 95 °C cure) to copper wires. The devices are tested in a custom made triple layer mu-metal magnetically shielded box. Two pairs of Helmholtz coils provide AC and DC magnetic fields. The coils were calibrated by a Lakeshore magnetometer model HMMA-2504-VR. The AC coil is powered by a Keithley 6221 AC current source operating at 20 Hz. The DC coil is supplied by an Agilent E3614A current source. The voltage on the ME device is measured by an SRS SR830 Lock-in amplifier.

III. Optimization

A. Interface Quality

The coupling between the magnetostrictive component and piezoelectric must be as ideal as possible to realize the full potential of the ME laminate. The effect of epoxy thickness and Young's modulus is studied in COMSOL 5.2 Multiphysics software. It can be seen from Fig. 2(a) that as the thickness of epoxy is reduced, the stress coupling to the PZT becomes better as the average stress increases for Young's Modulus of 1–12 GPa. However, the average stress is seen to peak for a Young's Modulus between 5–10 GPa, depending on the epoxy thickness as seen in Fig. 2(b), due to a trade-off between the epoxy not transferring strain when it is too compliant and reduction in strain when the epoxy is stiff.

A conductive silver epoxy with a Young's modulus of 6 GPa is chosen for these experiments [12]. Applying the epoxy without clamping during the cure results in a relatively thickness of 10–17 μm and porous film as seen in the scanning electron micrograph (SEM) cross section shown in Fig.3(a).

Applying a clamp during the cure reduced the thickness to 3–9 μm with clearly reduced porosity in the epoxy layer as seen in Fig. 3(b). This resulted in a significantly improved α_{ME} of 2.02 V/cm-Oe compared to 0.32 V/cm-Oe for non-clamped curing. All further tests in this manuscript use the clamped curing method.

B. Metglas® Annealing

We explore the α_{ME} enhancement though annealing of the Metglas® 2605SA1 by varying the anneal temperatures from 250 to 400 °C with and without a magnetic poling of 1600 Oe which is achieved by straddling two high temperature SmCo permanent magnets around the heater. The 1600 Oe field strength was confirmed using a magnetometer during a 400 °C anneal and at room temperature.

Fig. 4(a) shows the α_{ME} for 5 minute anneals with and without a magnetic field. The α_{ME} begins to increase above 300 °C from 2.02 V/cm-Oe for the as-cast (no anneal) sample to 5.1 V/cm-Oe for the 5 minute 400 °C anneal. However, there appears to be no significant difference with or without the presence of a 1600 Oe magnetic field. The improvement from these 5 minute anneals is considered to primarily arise from the reduction of residual stress in Metglas®.

Previous studies have shown that aligning the magnetic domains perpendicular to the applied field being sensed improves magnetostriction [10]. The maximum possible improvement in magnetostriction from a randomly aligned film can be determined by the engineering magnetostriction equation [13]:

$$\lambda = \frac{3}{2}\lambda_s\left(\cos^2\theta_f - \cos^2\theta_i\right) \quad (2)$$

where θ_i and θ_f are the initial and final magnetization angles relative to the applied magnetic field and λ_s is the saturation magnetostriction for an isotopically (randomly) aligned magnetic sample. For the case of domains aligned perfectly perpendicular to the applied field $\theta_i = \pi/2$ and then being perfectly aligned to the applied field during saturation $\theta_f = 0$, the maximum magnetostriction is $3/2\lambda_s$. This suggests that the improvement in α_{ME} performance due to Metglas® domain alignment from an isotropic to perpendicular case is 50%.

In an attempt to improve the domain alignment, the samples were annealed for 15 and 30 minutes in atmosphere at 350 and 400 °C with a 1600 Oe magnetic field. However, this resulted in decreasing α_{ME} with increasing Metglas® anneal times, as shown in Fig. 4(b). Annealing in a 10 Torr vacuum in a 1600 Oe for 5 minutes had no significant improvement over the atmospheric anneal. However, by annealing for 30 and 60 minutes in vacuum, an α_{ME} of 6.08 and 5.78 V/cm-Oe was measured, an improvement of approximately 20% from the 5 minute 400 °C anneal as shown in Fig. 4(b). We speculate this improvement is from magnetic domain alignment achieved from longer magnetic poling times and decreased oxidation due to the vacuum.

C. DC Electric Field Biasing

Electric field biasing of the PZT-5A modifies the d_{31} coefficient and thus improves α_{ME}. A 30 minute vacuum annealed and magnetically poled Metglas®-PZT device is DC electric field biased to alter the d_{31} coefficient. Fig. 5 shows the magnetostriction curve under as a function of the applied magnetic field for an applied dc electric fields from −2 to +2 kV/cm (limited by the maximum DC voltage permitted on the lock-in amplifier). At +2 kV/cm α_{ME} increases by 59% to 9.52 V/cm-Oe from the no electric field α_{ME} of 5.98 V/cm-Oe and at −2kV/cm α_{ME} decreases 50% to 3.02 V/cm-Oe. The increased α_{ME} of 9.52 V/cm-Oe, enables an improved lower detection limit in ME magnetic field sensing. The improvement in sensitivity due to the optimization described in this work are shown in Fig. 6. For a 20 Hz AC magnetic signal, the sensitivity increased from 6 nT for the initial device to 150 pT for the optimized device.

In conclusion, a significant improvement in α_{ME} from 0.32 to 9.52 V/cm-Oe has been achieved by optimizing the ME laminate, yielding a sensitivity improvement from 6 nT to 150 pT. We have shown through simulation and experimental results that mechanical coupling of the laminate is optimized by thinning the epoxy and reducing porosity via a clamp during curing. Next, an optimized anneal step for the Metglas® film which reduced the residual stress and aligned the magnetic domains was implemented with a 30 minute, 400 °C anneal in vacuum. A further improvement in the α_{ME} of the laminate was achieved by operating the PZT-5A under a 2 kV/cm DC electric field bias through an increase in the d_{31} coefficient during testing. Future work will incorporate PMN-PT with d_{33} mode sensing and an optimized number of Metglas® layers to further improve sensitivity.

Acknowledgments

This work was supported by the National Institutes of Health (NIH) under the Grant No. 1 R21 EY026438–01.

References

[1]. Wang Y, Gray D, Berry D, Gao J, Li M, Li J, and Viehland D, “An extremely low equivalent magnetic noise magnetoelectric sensor,” Adv. Mater, vol. 23, no. 35, pp. 4111–4114, 2011. [PubMed: 21800379]

[2]. Hatipoglu G and Tadigadapa S, “Experimental studies in magnetically induced transverse force-frequency effect in thin quartz microresonators,” J. Appl. phys, vol. 118, no. 3, p. 034508, 2015.

[3]. Tian J, Han P, and Payne D, “Measurements Along the Growth Direction of PMN-PT Crystals: Dielectric, Piezoelectric, and Elastic Properties,” IEEE Trans. Ultrason. Ferroelectr. Freq. Control, vol. 54, no. 9, pp. 1895–1902, Sep. 2007. [PubMed: 17941396]

[4]. Erturk A and Inmann JD, “Piezoelectric Energy Harvesting,” in Piezoelectric Energy Harvesting, 2011, p. 373.

[5]. Liu G, Nan CW, Cai N, and Lin Y, “Dependence of giant magnetoelectric effect on interfacial bonding for multiferroic laminated composites of rare-earth-iron alloys and lead-zirconate-tltanate,” J. Appl. Phys, vol. 95, no. 5, pp. 2660–2664, 2004.

[6]. Nan CW, Liu G, and Lin Y, “Influence of interfacial bonding on giant magnetoelectric response of multiferroic laminated composites of Tb1-xDyxFe2 and PbZrxTi1-xO3,” Appl. Phys. Lett, vol. 83, no. 21, pp. 4366–4368, 2003.

[7]. Filippov DA, Galichyan TA, and Laletin VM, “Influence of an interlayer bonding on the magnetoelectric effect in the layered magnetostrictive-piezoelectric structure,” Appl. Phys. A Mater. Sci. Process, vol. 116, no. 4, pp. 2167–2171, 2014.

[8]. Fang Z, Lu SG, Li F, Datta S, Zhang QM, and El Tahchi M, “Enhancing the magnetoelectric response of Metglas/polyvinylidene fluoride laminates by exploiting the flux concentration effect,” Appl. Phys. Lett, vol. 95, no. 11, pp. 1–4, 2009.

[9]. Das J, Gao J, Xing Z, Li JF, and Viehland D, “Enhancement in the field sensitivity of magnetoelectric laminate heterostructures,” Appl. Phys. Lett, vol. 95, no. 9, pp. 14–17, 2009.

[10]. Bucholtz F, Koo KP, Dandridge A, and Sigel GH, “Easy axis distribution in transversely annealed Metglas 2605 S2,” J. Magn. Magn. Mater, vol. 54–57, pp. 1607–1608, Feb. 1986.

[11]. Yang Y, Gao J, Wang Z, Li M, Li JF, Das J, and Viehland D, “Effect of heat treatment on the properties of Metglas foils, and laminated magnetoelectric composites made thereof,” Mater. Res. Bull, vol. 46, no. 2, pp. 266–270, 2011.

[12]. Epoxy Technology, “EPO-TEK H20E Technical Data Sheet,” 2015.

[13]. Datta A, Nathasingh D, Martis RJ, Flanders PJ, and Graham CD, “Saturation and engineering magnetostriction of an iron-base amorphous alloy for power applications,” J. Appl. Phys, vol. 55, no. 6, pp. 17841786, 1984.

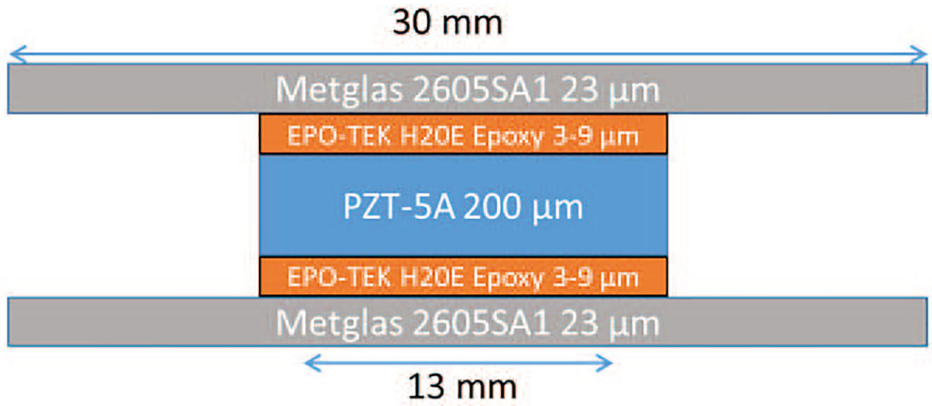

Fig. 1.
Illustrated cross section of ME device.

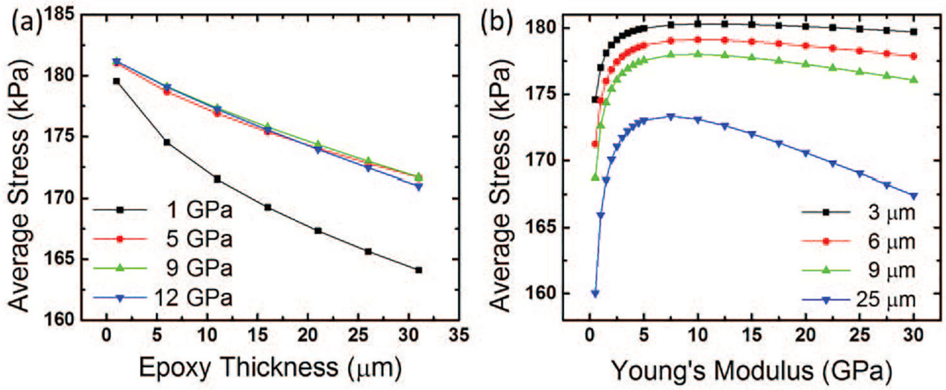

Fig. 2.

(a) Average stress coupling as a function of epoxy thickness with varying Young's Modulus values from 1–12 GPa shows thinner films are more effective at stress coupling. (b) Average stress coupling versus epoxy Young's modulus shows an optimal Young's modulus of 5–10 GPa, depending on epoxy thickness.

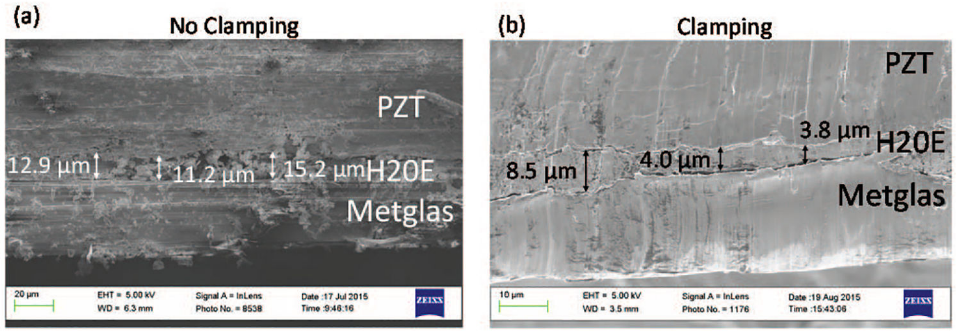

Fig. 3.

SEM cross sections of devices: (a) constructed with manual application of H20E without clamping results in a 10–17 um thick and porous interface. (b) Constructed with clamping during the cure results in a thinner, 3–9 um thick and non-porous H20E epoxy interface.

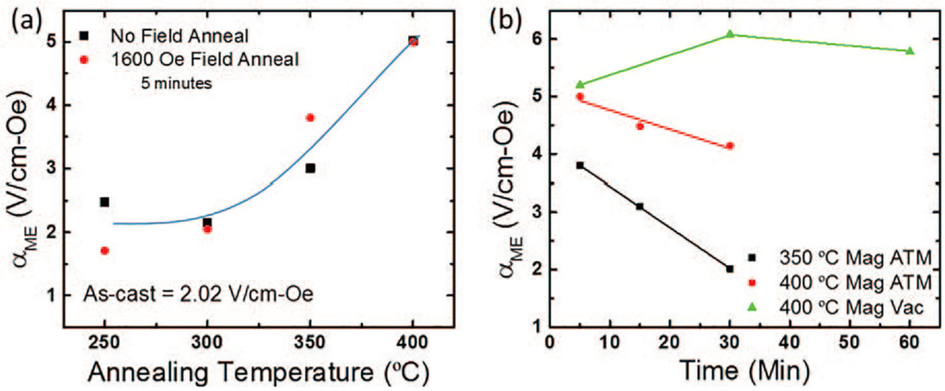

Fig. 4.

(a) α_{ME} -with and without a 1600 Oe magnetic field for a 5 minute anneal. The magnetic field does not significantly improve the α_{ME} for short anneals. (b) Longer anneals in atmosphere reduce the α_{ME}. Longer anneals in vacuum result in improved α_{ME} of 6.0 V/cm-Oe.

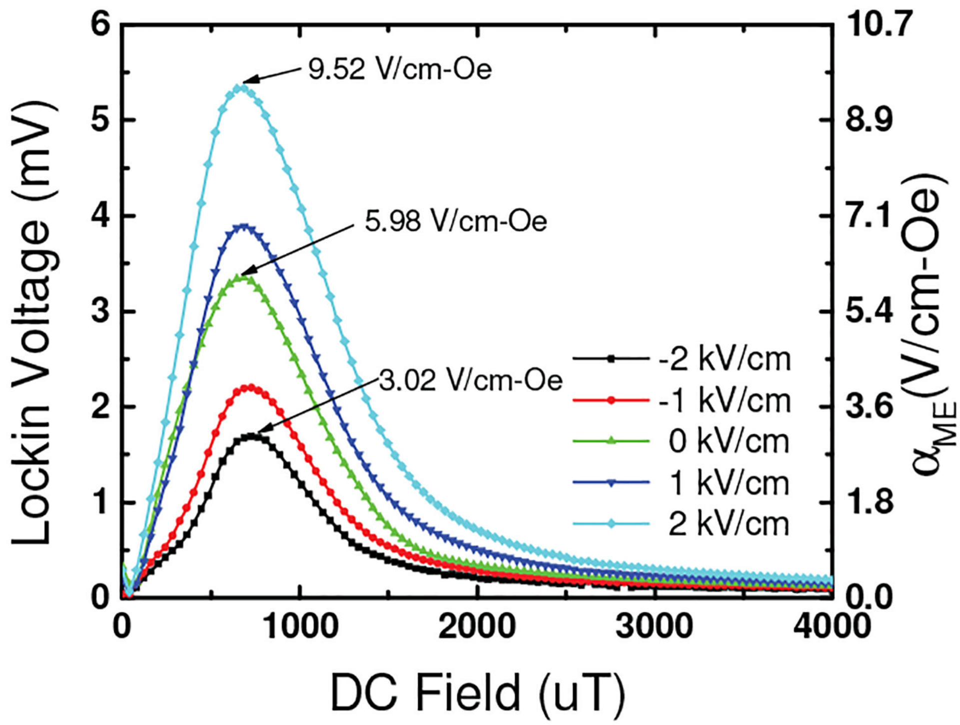

Fig. 5.

Magnetostriction curves under a DC electric field bias measured under a 2.8 uT AC field at 20 Hz. A 59% improvement is observed with a 2 kV/cm electric field.

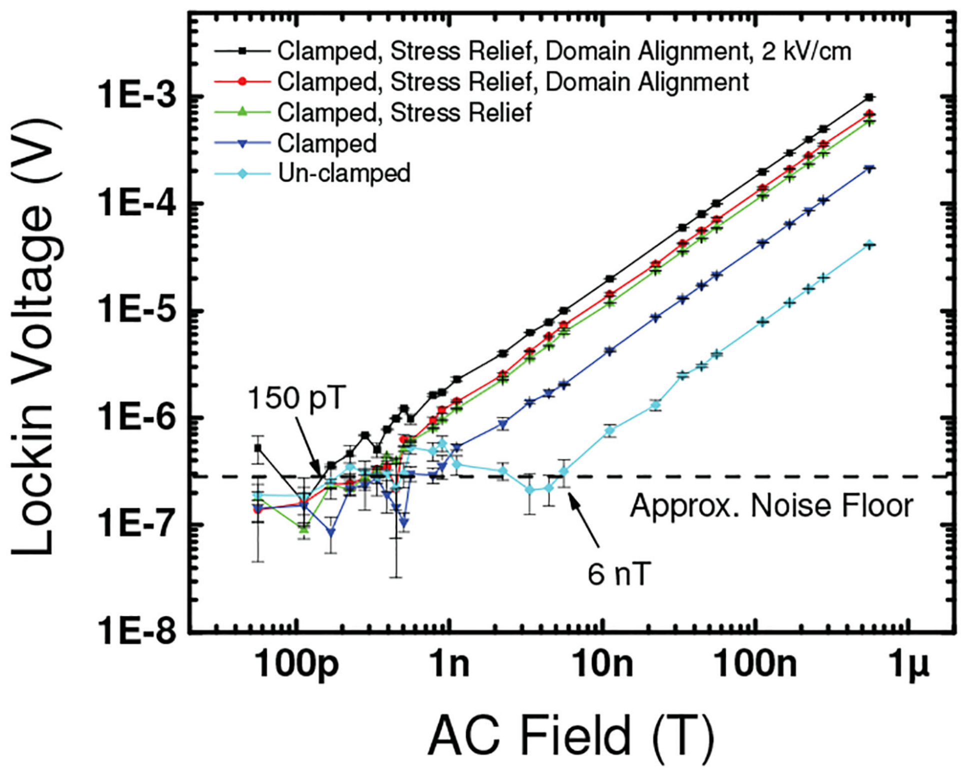

Fig. 6.

Measured lock-in voltage for decreasing 20 Hz AC magnetic showing an improvement in sensitivity from 6 nT in the un-optimized sample to 150 pT in the optimized sample with no observable change in the noise floor.