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Ba-hexaferrite films for next generation microwave devices (invited)

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Next generation magnetic microwave devices require ferrite films to be thick ($>300\ \mu$m), self-biased (high remanent magnetization), and low loss in the microwave and millimeter wave bands. Here we examine recent advances in the processing of thick Ba-hexaferrite (M-type) films using pulsed laser deposition (PLD), liquid-phase epitaxy, and screen printing. These techniques are compared and contrasted as to their suitability for microwave materials processing and industrial production. Recent advances include the PLD growth of BaM on wide-band-gap semiconductor substrates and the development of thick, self-biased, low-loss BaM films by screen printing. *© 2006 American Institute of Physics*. [DOI: 10.1063/1.2165145]

INTRODUCTION

Driven by radar electronics and wireless technologies, the next generation of magnetic microwave devices (isolators, filters, phase shifters, and circulators and related components) will be planar, self-biased, and low loss, and operate well beyond the performance metrics of today's devices. Self-biasing is an important property that eliminates the need for a biasing field that is provided by a comparatively large permanent magnet. The elimination of this magnet is an essential step in making these devices smaller and planar. Integration with semiconductor devices continues to be a desirable property that requires ferrite fabrication techniques to be compatible with complementary metal-oxide semiconductor (CMOS) processing. This is a difficult task considering that most ferrite fabrication techniques require temperatures $>900\ ^\circ$C to produce high-quality films.

In order to achieve these goals, magnetic materials must possess high saturation magnetization ($4\pi M_s$), high remanent magnetization (M_r), adjustable magnetic anisotropy fields (H_A), low microwave losses [i.e., low ferromagnetic resonance (FMR) linewidths ΔH_{FMR}], and for many applications, have the easy axis of magnetization perpendicular to the film plane (i.e., perpendicular magnetic anisotropy). In physical terms, the films should be thick ($>300\ \mu$m), dense (low levels of porosity that are responsible for added microwave loss), and pure phase. For many applications the microstructure should possess a strong crystallographic orientation, although true epitaxy is not required.

In this paper, we focus on recent advances made in the processing of Ba hexaferrite films for applications in microwave and millimeter-wave devices, with special emphasis on circulator devices. We will compare and contrast different film processing technologies including pulsed laser deposition (PLD), liquid-phase epitaxy (LPE), and screen printing.

Ba (M-type) hexaferrite (henceforth BaM) has the magnetoplumbite structure and a stoichiometry of $BaFe_{12}O_{19}$. This structure has 32 atoms/f.u. and 64 atoms in a single unit cell (see Fig. 1). One property of this compound that is of particular value in microwave device design is the strong uniaxial anisotropy with the easy direction being along the c axis ($H_A \sim 17\,000$ Oe).[1,2] The high magnetic anisotropy field can be adjusted by appropriate substitution for Fe and Ba ions allowing for the tuning of resonance frequencies from 1–100 GHz.[3] This degree of freedom makes BaM a choice material for many monolithic microwave integrated circuit (MMIC) applications.

The BaM structure consists of seven ferric ions distributed onto five interstitial sites (one trigonal bipyramidal, two octahedral, and two tetrahedral). The magnetism arises from the superexchange interaction between ferric cations mediated by the oxygen anion. This is a negative exchange interaction (i.e., ferrimagnetism or antiferromagnetism) with an amplitude from each Fe–O–Fe pairing dependent upon the angle made between the ferric cations and oxygen (i.e., larger exchange for larger angles). The magnetization (M_s) is reported to be 370 G with a Neél temperature of 450 °C and an FMR linewidth for a single crystal ranging from 10 and 20 Oe.[2,4] This compound is stable in air.

Ferrite circulator designs employ a bulk polycrystalline compact together with a permanent magnet for the necessary biasing field to saturate the compact along the perpendicular direction. When the compacts are processed following ceramic methods they possess relatively low to moderate hys-

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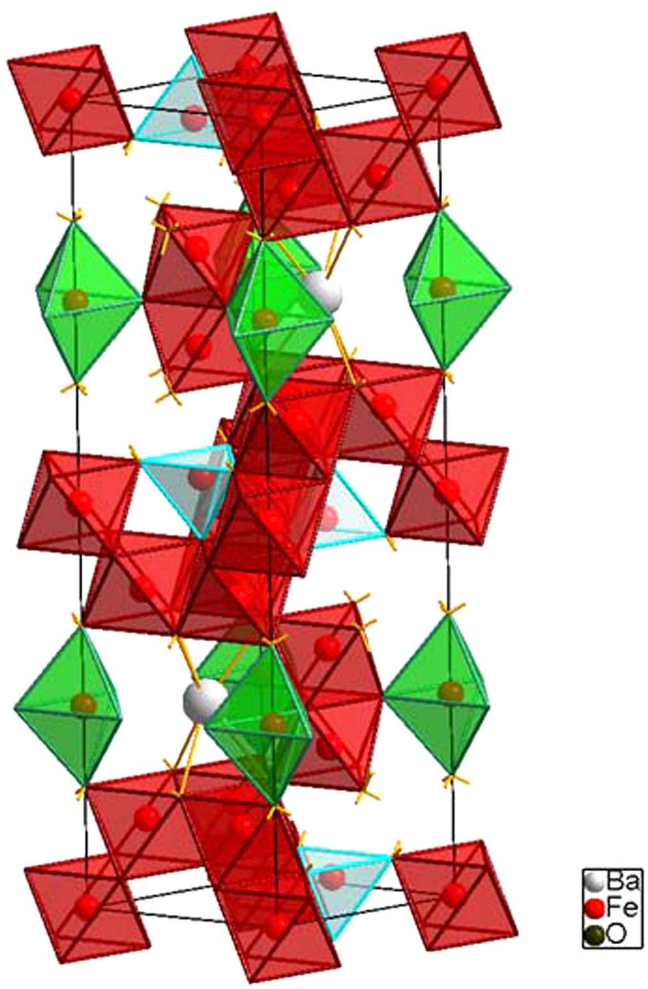

FIG. 1. (Color online) Schematic diagram of the Ba-hexaferrite *M*-type structure. Ferric cations are depicted as residing in five sites depicted as tetrahedral, octahedral, and trigonal bipyramidal.

teresis loop squareness (M_r/M_s) and FMR linewidths of ~2000 Oe.[5] However, Dionne and Fitzgerald have shown that in In-doped Ba*M* the use of a magnetic field during compaction provided hysteresis loop squareness values >0.90. With such hysteresis loop squareness values, these compacts may exhibit self-biased properties for circulator applications. (Note: With the substitution of In for Fe the magnetic anisotropy field reduces dramatically lowering the zero-field resonance frequency and redefining the device operational frequency and bandwidth.) Much research activity from 1990 to the present has focused on the development of Ba*M* as thin and thick films. The processing of Ba*M* films have been performed using pulsed laser deposition, sputter deposition, liquid-phase epitaxy, and more recently screen printing.

PULSED LASER DEPOSITION

PLD is a well-accepted method for processing films of oxide materials. In its most traditional application an Excimer laser is used to ablate a molecular flux from a homogeneous target. The ablated flux is intercepted by a substrate that is often held at a high temperature to allow for the necessary adatom mobility for the near-equilibrium growth of the target material as a film. A demonstration of PLD growth of Ba*M* was made by Dorsey *et al.*[6] in 1992 [although the patent for this process was awarded to Vittoria in 1990 (Ref. 7)]. Those films were shown to have derivative linewidths as low as 66 Oe at 58 GHz. Since then there have been many groups that have grown Ba*M* via PLD.[8–10] Song *et al.*[9] have reported half power linewidths of Ba*M* grown on sapphire as low as 27 Oe at 60.3 GHz. Over time it has been shown that the best quality films correspond to high-temperature growth (>900 °C) on lattice-matched substrates (sapphire, Al_2O_3, MgO, GdGa-garnet (GGG), etc.). Figure 2 are hysteresis loops from Ref. 9 showing clearly the uniaxial perpendicular anisotropy with an anisotropy field of ~17 000 Oe which is in good agreement with the bulk value.[11] The magnetic easy axis, aligned perpendicular to the film plane, is a useful property for circulator device applications. By inspection of Fig. 2, the easy loops are sheared from the effects of the demagnetizing energy resulting in near-zero remanence and thus, although possessing a very high crystal quality, these films are not self-biased. Like most ferrite processing techniques, PLD requires that ferrites be grown at temperatures >900 °C. At these temperatures one can expect the degradation of most semiconductor substrates. Exceptions are the recently developed wide-band-gap materials SiC and GaN.

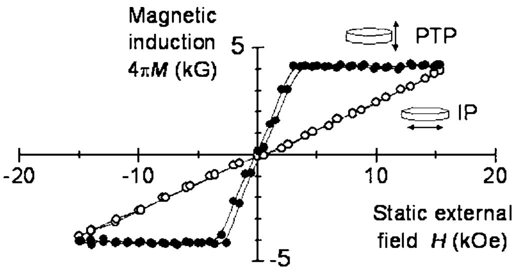

FIG. 2. Hysteresis loops of a PLD grown Ba*M* film showing perpendicular magnetic anisotropy with an anisotropy field of ~17 000 Oe. (after Ref. 9; reproduced with the permission of the authors).

Recently, Chen *et al.*[12] have demonstrated the growth of Ba*M* on single crystal 6H–SiC. Previous attempts to grow ferrites on semiconductors (i.e., Si and GaAs) have lead to degradation of the substrate by alloying and decomposition, respectively. In SiC one has a substrate that can withstand the high temperatures required for the growth of high quality (i.e., low-loss) Ba*M*.

All the films produced by Chen *et al.* showed a clear hexagonal crystal x-ray-diffraction pattern [see Fig. 3(c)]. An atomic force microscopy (AFM) image is displayed as Fig. 3(a) for the sample grown at 20 mTorr of oxygen pressure. At low oxygen pressures the images illustrate large hexagonal crystals (typically 1 μm in diameter) with their *c* axes oriented normal to the film plane. Magnetic hysteresis loops [$4\pi M$ (G) vs H_{app} (Oe)] for films deposited at 20 mTorr oxygen pressure are presented as Fig. 3(b). In these data the easy magnetic axis is aligned perpendicular to the film plane and the hard axis in the film plane. It is noteworthy that the squareness values increased with increasing oxygen pressure reaching a maximum of ~0.7.

At low oxygen pressures the structure of the growing film is prone to anion defects that lead to a reduction in the

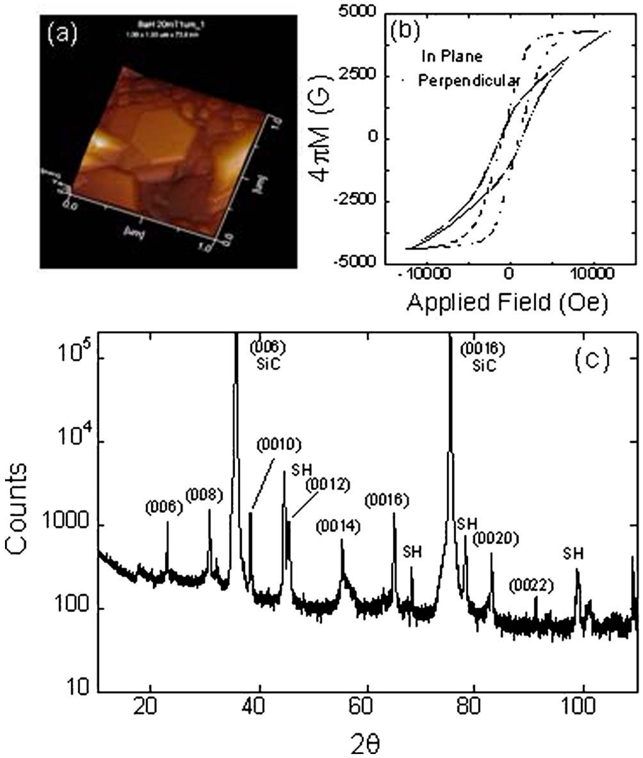

FIG. 3. (Color online) (a) Atomic force microscopy image of a Ba*M* film grown via PLD on single-crystal 6H–SiC substrates collected in tapping mode illustrating hexagonal crystals oriented with the *c* axis perpendicular to the film plane; (b) hysteresis loops obtained by vibrating-sample magnetometry; and (c) XRD spectrum illustrating a strong $(0,0,2n)$ crystal texture (SH=substrate holder). The film was deposited in 20 mTorr O_2 and at a substrate temperature of 925 °C (after Ref. 12; reproduced with the permission of the authors).

superexchange interactions and magnetization.[13] The magnetization increased to near its bulk value corresponding to $p_{\mathrm{ox}} \sim 20$ mTorr, signaling a reduction in anion defects. Ba*M* films deposited on 6H–SiC by PLD showed an iron deficient surface consistent with Kamzin *et al.*[14] X-ray photoemission spectroscopy (XPS) depth profiling showed a small amount of silicon throughout the Ba*M* film, suggesting that there may be diffusion across the interfacial region. Both the depth profiling and the analysis of very thin Ba*M* films suggest the possibility of a barium-rich interface.

Although PLD has been shown to produce high crystal quality films having perpendicular magnetic anisotropy and low microwave losses, the thicknesses are as much as an order of magnitude too thin for practical microwave devices. In addition, most PLD systems are research tools that deposit over limited diameter substrates (<50 mm). Production tools, allowing for large area deposition and high throughput, are not prevalent. For the processing of thicker films of high crystal quality researchers have turned to liquid-phase epitaxy.

LIQUID PHASE EPITAXY

In liquid-phase epitaxy of Ba*M* films, a single-crystal seed is lowered into a molten solution, typically of a boron-based Ba-hexaferrite composition. The seed, typically a single-crystal lattice-matched substrate, i.e., MgO, sapphire, GGG, etc., is rotated, and the melt temperature is slowly reduced through a liquidus transition.

As the liquidus temperature is passed, a crystal is nucleated on the substrate and grows during the reduction in melt temperature. Growth rates have been shown to be dependent upon the substrate and can range from a few to $>100\ \mu\mathrm{m/h}$.[15–17] Figure 4(a) is a scanning electron microscopy (SEM) image of the surface of an LPE film on a GGG substrate illustrating large hexagonal crystallites ($\sim$10–20 μm) oriented with the *c* axis perpendicular to the film plane.[17] The XRD spectrum for this sample [Fig. 4(c)] shows clearly the strong $(0,0,2n)$ texture relative to the GGG (111) with a rocking curve full width at half maximum (FWHM) (inset) of 0.05°.[16] The FMR linewidth, as the peak to peak of the power derivative, is measured to be as low as 28 Oe for samples having perpendicular anisotropy (on MgO) and 75 Oe for the in-plane films (on sapphire). Vibrating-sample magnetometer (VSM) hysteresis loops for the Ba*M* on GGG are presented in Fig. 4(b). One sees a clear uniaxial perpendicular anisotropy with small coercivities and $H_A \sim 17$ kOe. Once again, the remanent magnetization was low, and therefore these films were not self-biased.

Ba*M* films have been grown by LPE as thick as 200 μm.[16] The growth of films thicker than $\sim$150 μm suffer from cracks arising from mismatches in the thermal-expansion coefficients. At these thicknesses, Ba*M* films are more attractive than PLD films for applications in microwave devices but are still not ideal. (Practical microwave devices require thicknesses in excess of 300 μm.) Other shortcomings of LPE are the difficulties and costs associated with upgrading this technique to production units capable of high throughput. Even with these detractions, LPE remains a preferred technique for producing high-quality, thick BaM films.

A third technique for producing thick films of ferrites is screen printing. Screen printing technology is capable of producing films in excess of 1 mm thick. In the modern electronics industry, this technique is usually applied in producing thick-film circuits and sensors. Remarkably, this technique has not until recently been extended to fabricate textured ferrite thick films for microwave applications.

SCREEN PRINTING

Recently, Chen *et al.*[18] have demonstrated that screen printing is a technique capable of processing thick, self-biased, low-loss Ba*M* films.

In this technique, pure phase Ba-hexaferrite powders are mixed with a binder to form a suitable paste for printing. The printing is done through a template or mask. In the work by Chen *et al.*, the still wet film was baked at 250 °C to burnout the binder. During this low-temperature annealing a dc magnetic field was applied perpendicular to the plane of the film. A second heat treatment at $\sim$1200 °C was required for recrystallization and sintering. Figures 5(a) and 5(b) are SEM images of a screen-printed film surface morphology and cross section after the films had been sintered, respectively. Prior to sintering, micron-sized particles were loosely ar-

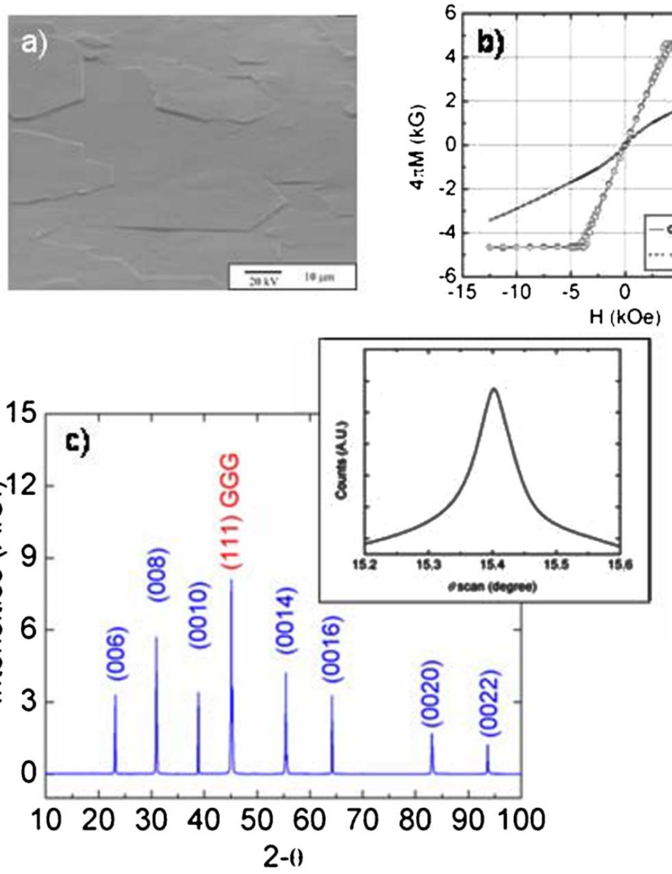

FIG. 4. (Color online) (a) SEM image of the surface morphology of a LPE-grown 45 μm Ba*M* film on (111) GGG; (b) hysteresis loops of the same film illustrating the perpendicular magnetic anisotropy and anisotropy field ~17 000 Oe; and (c) the XRD spectrum illustrating strong crystal texture $(0,0,2n)$ and the rocking curve of the (008) peak (after Ref. 17; reproduced with the permission of the authors).

ranged with the film having very high porosity (~50%). After sintering [Fig. 5(a)], the film had a closely packed polycrystalline structure in which hexagonal grains range in size from ~1 to 10 μm with porosity levels of 13–15%. In Fig. 5(b), the structure of the film is revealed to contain elongated grains with the long axis parallel to the film plane. Some pores remain visible. XRD analysis of this sample displayed $(0,0,2n)$ reflections having enhanced intensity consistent with *c*-axis texture perpendicular to the film plane. In Fig. 6 are hysteresis loops that display the characteristic perpendicular magnetic anisotropy. In comparison to the PLD

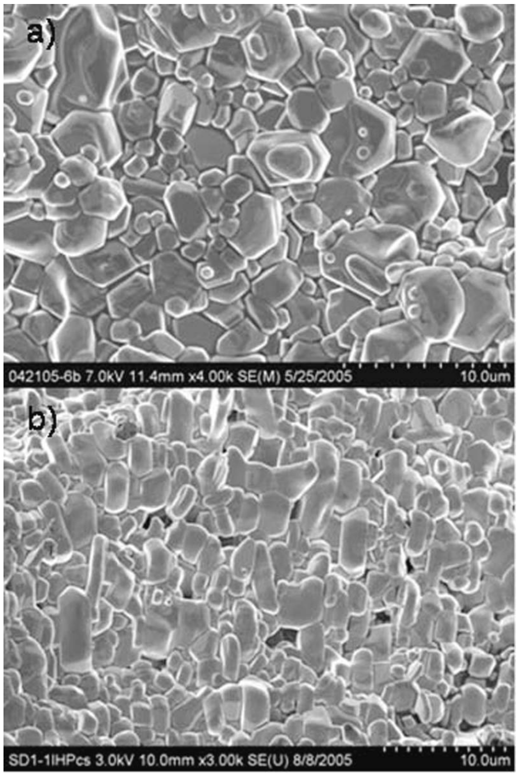

FIG. 5. (a) SEM image of the surface morphology of a screen-printed Ba*M* film after burnout and sintering procedures. (b) SEM cross section of the same film illustrating elongated grains oriented with their long axis parallel to the film plane (after Ref. 18; reproduced with the permission of the authors).

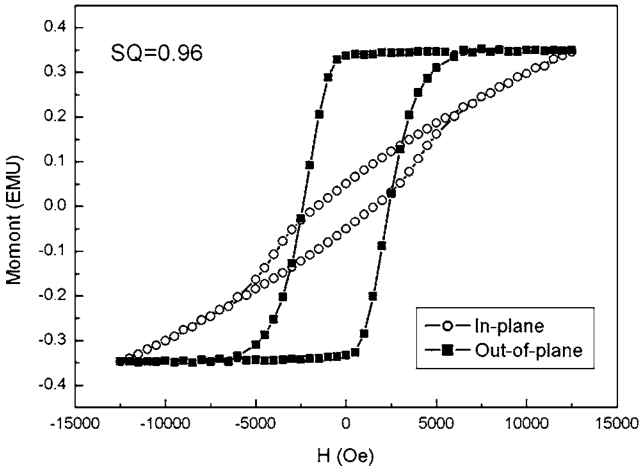

FIG. 6. Typical hysteresis loops for screen-printed films illustrating high loop squareness for the easy axis loop perpendicular to the film plane (after Ref. 18; reproduced with the permission of the authors).

TABLE I. Comparison of different Ba*M* processing techniques.

Technique	Self-bias (M_r/M_s)	FMR linewidth (Oe)	Film thickness (μm)	Industrial processing cost	Device volume
Compacts	>0.9	2000–3000	>1000	Low	High
PLD	$<0.2;0.7^a$	~ 27	10's	High	High^b
LPE	<0.2	$\sim 30^c$	<200	High	High^b
SP	>0.95	$<200^c$	>500	Low	Low

[a] Ba*M* grown on SiC has demonstrated a 0.7 squareness for some growth conditions. High-quality films grown by PLD on MgO, GGG, sapphire, and Al_2O_3 are consistently <0.2.

[b] Volume remains large due to the need for large biasing magnet.

[c] Power derivative linewidths.

and LPE films, these films have higher coercivity but also very high hysteresis loop squareness (~ 0.95), providing these thick films with self-bias properties. FMR linewidths less than 210 Oe have been measured. Although large compared with PLD and LPE films, these values are small compared with polycrystalline compacts (typically >2000 Oe) and acceptable for many MMIC applications.

OUTLOOK

In reviewing these latest results of thick, oriented Ba*M* films, there is reason for optimism. Researchers have grown Ba*M* on a wide-band-gap semiconductor substrate (SiC) that is well suited for the high-temperature growth of ferrites. These thin films may be utilized as "seed" layers in the growth of thick single-crystal films by the LPE technique.[15] Hence, it is plausible to grow thick films on semiconductor substrates.

Table I allows a comparison between film processing techniques. LPE, and to a lesser degree PLD (for film thickness reasons), remain the primary techniques for processing near single-crystal quality BaM films as judged by crystallographic data and microwave loss. These films tend to have outstanding microwave properties with FMR linewidths of 25–30 Oe. Surprisingly, screen printing, long known as a crude method of film fabrication, has been shown to be capable of processing thick films of good microwave quality (FMR linewidths of <200 Oe). The loop squareness values exceed 0.95 demonstrating self-bias properties. However, much work is still needed to improve film density and to further reduce microwave loss. One outstanding issue remains the ability to process thick films having low microwave loss and self-biased properties. This so-called *self-biased paradox* calls for the growth of films having high crystal quality, translating to low microwave loss, and high remanence magnetization, typically corresponding to a state of high coercivity. In growing a film of high crystal quality one obtains a low coercivity, which together with the demagnetizing energy of a film, shears the easy axes loop resulting in low remanence. Many mechanisms that result in enhanced coercivity, e.g., grain boundaries, inhomogeneities, local anisotropy fields, pores, etc., increase microwave loss to unacceptable levels. Screen printing has shown to overcome this paradox. The fact that screen printing is suitable for large substrate and high throughput makes this technique attractive for industrial processing.

ACKNOWLEDGMENTS

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