Fabrication of a high-resolution roll for gravure printing of 2µm features

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ABSTRACT

High-resolution features are key to achieve high performance printed electronics devices such as transistors. Gravure printing is very promising to achieve high resolution in combination with high printing speeds on the order of 1m/s. High-speed gravure has recently been shown to print high resolution features down to linewidths and spacing of 2µm. Whilst this was a tremendous improvement over previous reports, these results had been obtained using silicon printing plates. These silicon printing plates are fabricated using microfabrication techniques which offer several advantages over traditional metal gravure cylinders where the features are defined by techniques such as stylus engraving, laser engraving or etching. This offers much greater precision and design freedom in terms of feature size, surface roughness, cell placement and cell shape. However, rigid silicon printing plates cannot be used in a roll-to-roll printing process that would truly enable low-cost printed electronics. Here we demonstrate for the first time a gravure printing roll that combines the precision of silicon printing plates with the form factor of a metal cylinder.

The fabrication process starts with a silicon master whose pattern is replicated by polymer molding. The actual metal printing plate is then built up on the polymer negative of the pattern by a combination of electroless and electroplating. After separation of the polymer and the metal, the metal printing plate can be mounted on a magnetic roll for printing. Printing of highly scaled 2µm features is demonstrated. Different metal surfaces were explored to optimize printing performance and wear during printing.

Keywords: Gravure printing, printed electronics, high-resolution printing, high-speed printing, gravure roll fabrication, hard layer, wear

1. INTRODUCTION

Printed electronics is an emerging technology that holds great promise to enable light-weight, low-cost, flexible electronics on substrates such as plastic or paper.[1–8] The main benefit of printed electronics is its additive nature that allows the deposition of materials in desired locations without the need for costly lithography and etching steps. If this is done at high speeds, truly low-cost devices and systems can be fabricated. Unfortunately, traditional techniques for high-speed printing such as screen or gravure printing have been limited in printing resolution to several tens of micrometers[9] whilst higher resolution roll-to-roll patterning techniques such as laser ablation have been limited in terms of throughput[10]. Recently, it has been shown that gravure can be pushed towards high-resolution printing below 5µm whilst maintaining printing speeds on the order of 1m/s.[11,12] Whilst this is a tremendous step forward, the best results have been obtained using silicon printing plates. These printing plates are fabricated using traditional microfabrication techniques including photolithography and dry and wet etching. This leads to superior control over critical factors compared with traditional techniques to fabricate gravure rolls such as stylus or laser engraving. These techniques reach their limits below about 10µm cell size.[13,14] It becomes increasingly difficult to accurately define cells in a gravure cylinder at these highly scaled dimensions and control over the cell shape becomes very limited. Additionally, the engraving process introduces severe roughness to the surface of the roll on a similar size scale as the smallest cells. This makes polishing unrealistic and thus print quality is severely impacted by the roll roughness. All of this is no issue when using silicon printing plates that allow very precise cell patterning using proven microfabrication techniques whilst maintaining the ultra-smooth surface of silicon wafers. However, the main drawback of silicon printing plates is their form factor. They cannot be used as a roll in a mass-production roll-to-roll or sheet-fed printer (see Figure 1 for an illustration of the roll-based gravure process). We have thus developed a process to transfer the surface of a silicon printing plate with its

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superior properties into a metal plate. This metal plate is then wrapped around a cylinder to be used as a roll for gravure printing. With this novel gravure roll we can achieve printing resolutions down to 2µm linewidths.

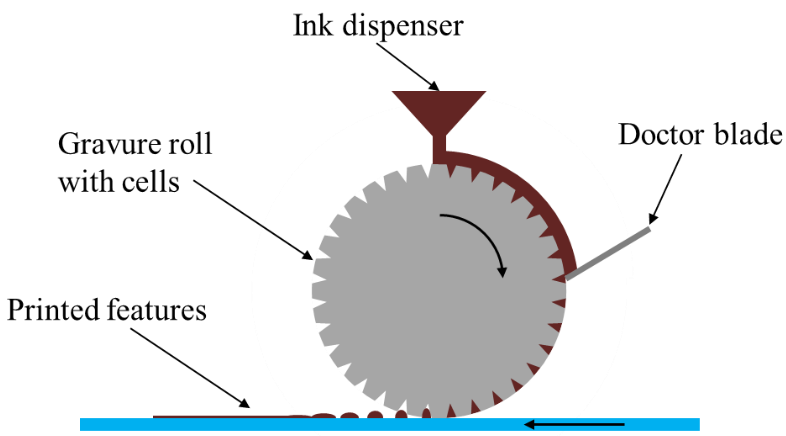


Figure 1. Illustration of the roll-based gravure process where the pattern is etched or engraved into a cylinder and the ink is transferred from the cells onto a flat substrate such as plastic or paper.

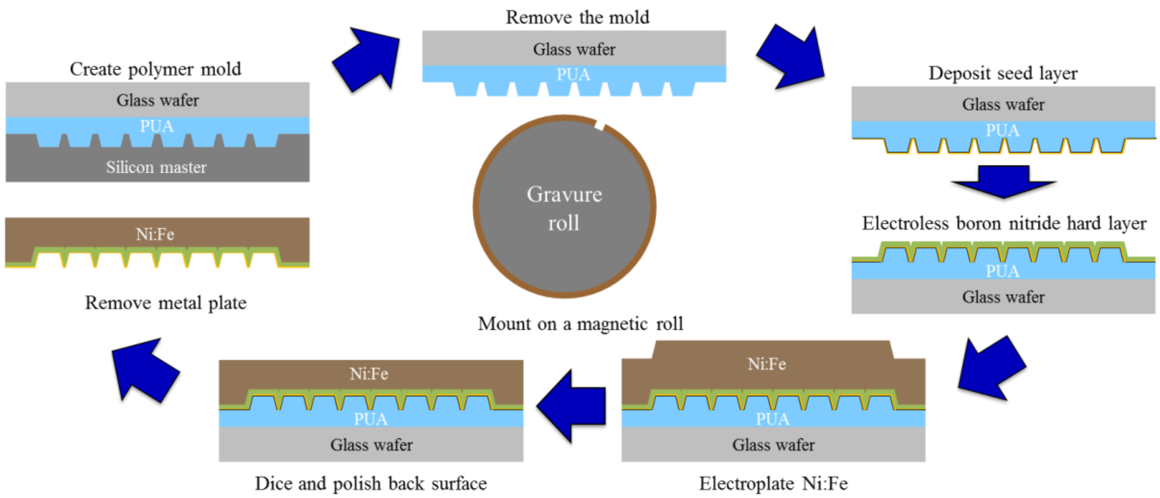
2. ROLL FABRICATION PROCESS

The first step in the roll fabrication process is the fabrication of the silicon master. Photolithography is used to define the cell features with a critical dimension of 250nm for the smallest cell gaps. The cells are then etched into the silicon using a silicon dioxide hard mask. Different cell shapes can be obtained by using different etching methods. Square cells are obtained using dry etching. Inverted pyramid shapes that resemble the shape obtained from stylus engraving can be obtained using KOH as the wet etchant for silicon. This limits the orientation of the cells to be aligned with the 110 crystal plane of the silicon wafer; however, this is not a significant limitation for most Manhattan style circuit layouts. The details of this process were published elsewhere.[11]

In order to fabricate the metal printing plate (see Figure 2 (a) for an overview of the process), the pattern is first transferred from the silicon master into a polymer through a molding step. After release of the polymer from the silicon mold, the polymer is metallized. First a chrome gold seed layer is evaporated. Then a hard surface layer of nickel with boron nitride particles is applied by electroless plating.[15,16] The electroless plating solution was purchased from Caswell Inc. On top of this the main thickness of the printing plate is built up using electroplating of permalloy (80% nickel, 20% iron).[17] Before release of the metal stack from the polymer molding, the backside of the metal is polished and the metal is diced into the shape of a rectangular printing plate. After release, the metal surface with the hard layer is a perfect replica of the silicon master (see Figure 3). The high magnetic permeability of the permalloy allows mounting of the printing plate on a magnetic roll ready for printing (see Figure 2 (b)).

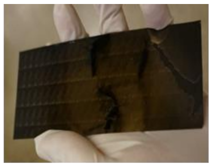
The choice of molding polymer is critical for the success of this process. Polyurethane acrylate (PUA, purchased from Minuta Technology Co.) works well both for the molding as well as the metallization steps.[18] Soft materials such as polydimethylsiloxane (PDMS) with a Young's modulus of 1-10MPa can be removed from the silicon master very easily after molding. The PDMS deforms readily as it is peeled away from the silicon master not putting any significant stress on the silicon. However, during metallization cracks are formed very easily in the metal layer on top of the soft polymer due to internal stresses in the metals. In addition, standard PDMS formulations are high viscosity (3500cP), which makes it more prone for bubble entrapment during the molding. On the other hand epoxy is a material that is hard enough for the metallization process (Young's modulus 1-10GPa). However, this leads to problems during the demolding step. Epoxy being optimized for adhesion needs significant force to be pulled away from the large area of a six inch wafer. This cannot be done by stepwise peeling as for PDMS due to the rigidity of the epoxy. This puts significant stresses on the silicon master as well as the epoxy mold leading to cracking. Similarly, thermal curing can lead to cracking due to thermal stresses and thus UV curing needs to be employed. PUA combines the benefits of both. Its hardness lies in between PDMS and epoxy at 300-1500MPa. Together with a low surface energy this enables easy demolding. However, it is sufficiently hard to prevent the formation of cracks during metallization. UV curing prevents the build-up of thermal stresses during curing. A low viscosity formulation (100-150cP) aids in bubble-free molding.

(a)



(b)

Metal plate



Wrap around magnetic roll

Figure 2. (a) Metal plate fabrication process starting from silicon master plate. (b) Final metal plate after polishing, dicing and lift-off from PUA mold ready to be wrapped around magnetic cylinder for printing.

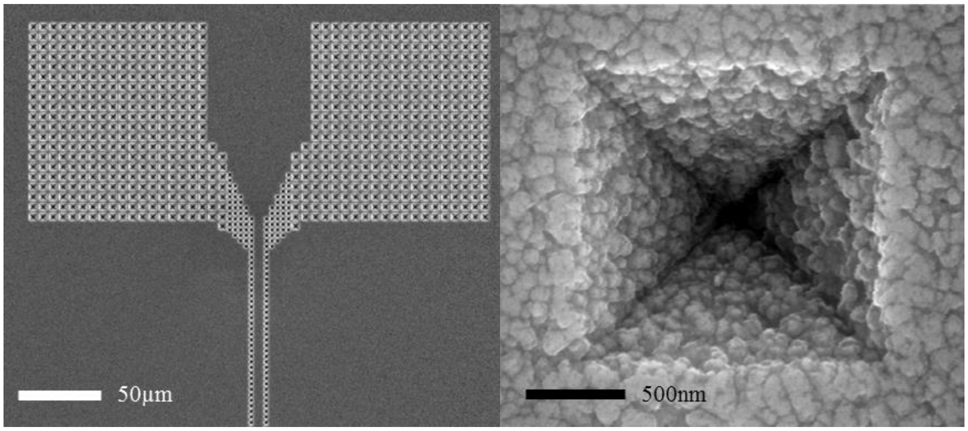


Figure 3. SEM images of cell features on metal printing plate at different magnifications. The inverted pyramid shape from KOH etching of the silicon master is clearly visible. One can observe the boron nitride particles making up the hard layer.

3. PRINTING RESULTS

Finally, after mounting of the metal printing plate on the magnetic cylinder, it can be used for printing of active materials such as polymer or nanoparticle based inks. In order to fully utilize the highly scaled features on the gravure roll, a deep understanding of the underlying physics of gravure printing is required. One needs to consider ink properties, printing speed, doctor blade properties, substrate wetting and roll wetting properties. Optimization of the wetting properties of the roll surface is enabled by the roll fabrication process proposed here. The hard layer on top of the main body of the plate can be modified to engineer the roll's surface properties. Here, we show two different surfaces: the bare nickel iron printing plate body and a boron nitride hard layer.

Print quality was optimized by varying capillary number $Ca = \frac{\mu U}{\gamma}$ where μ is ink viscosity, U is printing speed and γ is ink surface tension. This dimensionless quantity combines both ink parameters and the printing speed and determines the outcome of many of the sub-processes of the gravure printing process, namely cell filling, doctor blade wiping, drag-out and ink transfer to the substrate.[11] Ink spreading on the substrate on the other hand is determined by ink properties and surface properties of the substrate, not printing speed. Here we varied capillary number to optimize print quality. The ink used here was poly-4-vinyl phenol (PVP) dissolved in propylene glycol monomethyl ether acetate (PGMEA). PVP is a polymer dielectric commonly used in printed electronics.[19–21]

Printing optimization with hard layer

First consider printing with the boron nitride hard layer. One can observe a clear improvement in print quality as Ca is varied over more than one order of magnitude for a 146cP PVP ink (see Figure 4). At Ca=0.11 hardly any ink is printed onto the substrate. This improves substantially when Ca is increased to 1.1; however, one can still observe holes in printed rectangles as well as breaks in high resolution lines. These defects are removed when printing at Ca=5.4. The reason for this significant difference in print quality as Ca is increased is the reduction of drag-out. As the doctor blade passes over the cells, it picks out ink from the cells, which is subsequently re-deposited behind the printed feature. This leads to a reduction in ink volume in the printed feature as well as characteristic drag-out tails behind features. Both effects can be observed in the low-speed prints. At higher print speeds there is less time for ink to wick up the doctor blade thus reducing the detrimental effects of drag-out. Ca could not be increased further at this viscosity due to equipment limitations in terms of print speed. Large scale roll-to-roll gravure printers can print at higher print speeds that might lead to further improvements in print quality. Print quality will then become limited by lubrication residue from ink that passes through the small gap underneath the doctor blade. A higher viscosity ink could also be used to increase capillary number. However, the ink viscosity cannot be increased too much because of insufficient ink spreading on the substrate. Since ink needs to spread between individual drops produced by discrete cells, lines become discontinuous when ink viscosity is raised too much. With these optimized printing conditions the roll can then be used to print 2μm lines at a high speed of 1m/s as can be observed in Figure 5.

Printing optimization without hard layer

By leaving out the boron nitride hard layer, the top surface of the roll is simply the nickel iron that makes up the body of the plate. This changes the surfaces wetting characteristics of the roll and thus printing needs to be optimized separately. One can again observe improved print quality for initial increases in printing speed and capillary number from 1.1 to 2.1 due to the suppression of drag-out (see Figure 6). However, at Ca=4.2, one can also observe breaks in lines and holes in pads. In this case the printed ink volume is limited by the cell filling process. The ink requires time to fully fill the cells due to capillary forces. If Ca is too large, there is not enough time for this process to complete fully and air is entrapped in the cells.[22] Thus optimum printing without the boron nitride hard layer is achieved at Ca=2.1, which is lower than with the boron nitride surface where the transition into the filling limited regime was not observed up to Ca=5.4.

This difference can be explained by the different wetting properties of the two surfaces. Boron nitride is used as an extremely slick, low-friction, high lubricity surface coating. This manifests itself in a smaller contact angle hysteresis (Nickel iron: θ_R=25°, θ_A=90°. Boron nitride: θ_R=40°, θ_A=80°.), which enhances both cell filling and drag-out. Cell filling is enhanced by the lower advancing contact angle, which promotes the advancing of the ink meniscus into the cell during filling. Similarly ink can be pulled out from the cell more easily due to the larger receding contact angle. Thus the transition from the drag-out limited regime to the filling limited regime is shifted to higher capillary numbers for the roll with the born nitride hard layer. For the same viscosity this translates into higher printing speeds. This is an economic advantage in the manufacturing of printed electronics systems since throughput is increased by higher print speeds.

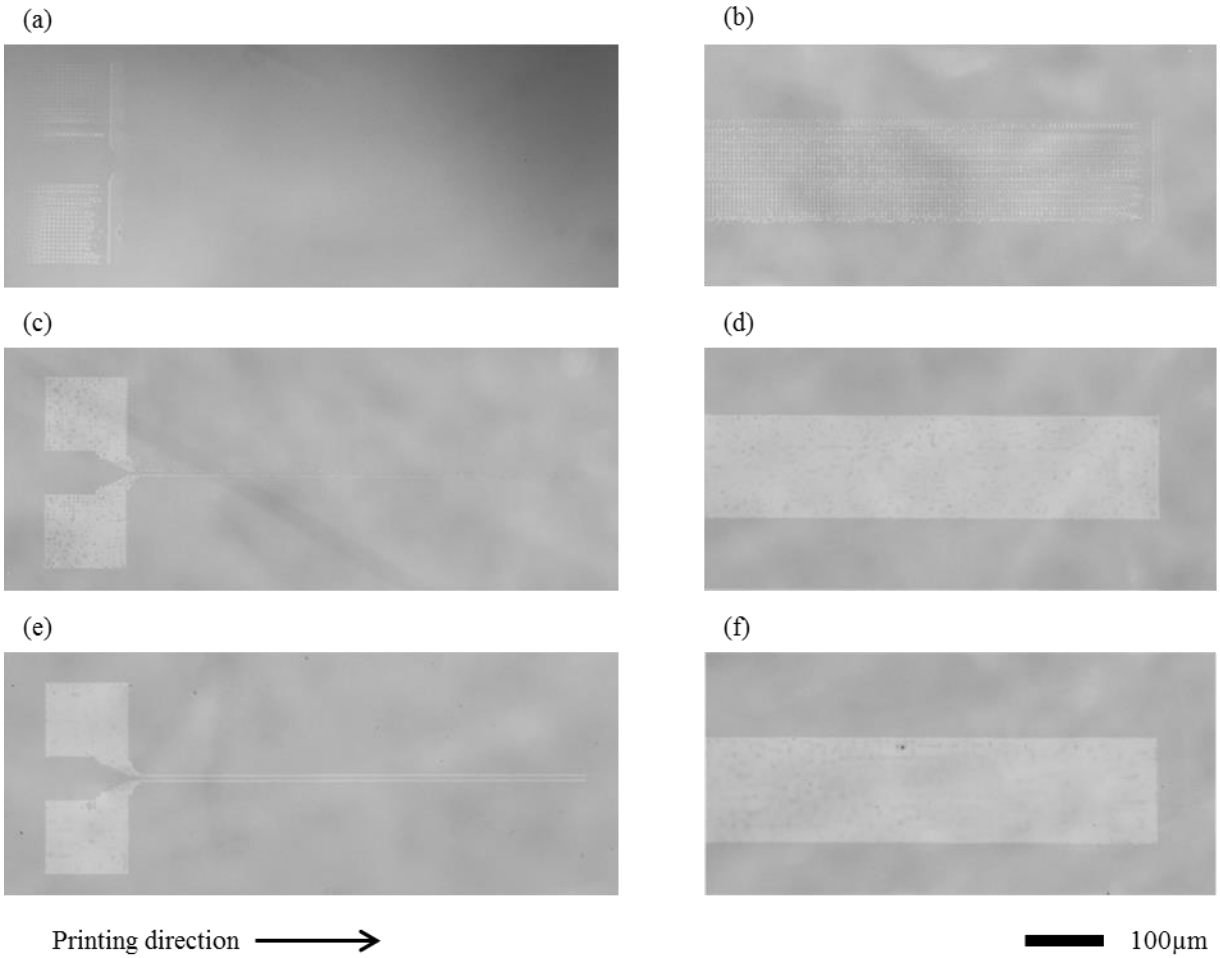


Figure 4. Printed features with hard layer. (a) & (b) Ca=0.11: thin 2µm lines do not print at all and large pads are mostly made up of isolated dots due to drag-out. (c) & (d) Ca=1.1: thin 2µm lines print partially and large pads have holes due to reduced drag-out. (e) & (f) Ca=5.4: thin 2µm lines as well as large pads print well due to the suppression of drag-out.

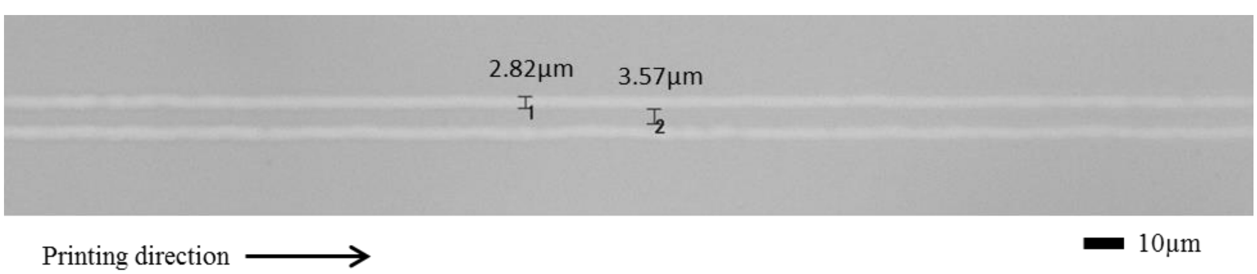


Figure 5. Parallel lines printed from 2µm cells resulting in continuous sub-3µm lines. Ca=5.4, ink viscosity 146cP, print speed 1.0m/s.

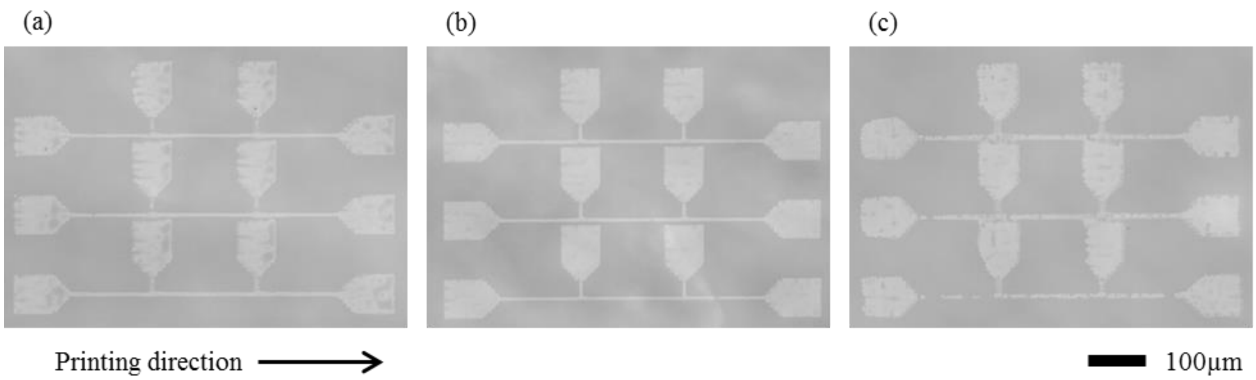


Figure 6. Printed features without hard layer. (a) Ca=1.1: Some holes in print due to drag-out. (b) Ca=2.1: Optimal printing at the cross-over point between the filling and drag-out limited regimes. (c) Ca=4.2: Significant gaps in lines due to insufficient filling of cells.

Effect of hard layer on roll scratching

One benefit of the boron nitride hard layer is the increase in print speed for optimal printing. The other main effect is the protection of the roll surface from scratching during printing. As the doctor blade, which is made from steel, presses down on the roll, it can produce scratches in the roll. This is especially true when the lubrication film between the doctor blade and the roll is minimized to enhance print quality.[23] This leads to increased roll surface roughness, which can affect print quality detrimentally. The roll surface is still scratched by the blade with the boron nitride hard layer; however, the steady state level of roughness after about 20 prints is reduced by the hard layer (see Figure 7). This improved roughness leads to better print quality as evidenced in Figure 8. The roll with the boron nitride hard layer still prints continuous lines after 50 prints. Conversely, lines printed with the roll without a hard layer exhibit some discontinuities after 50 prints due to the scratching of the roll surface.

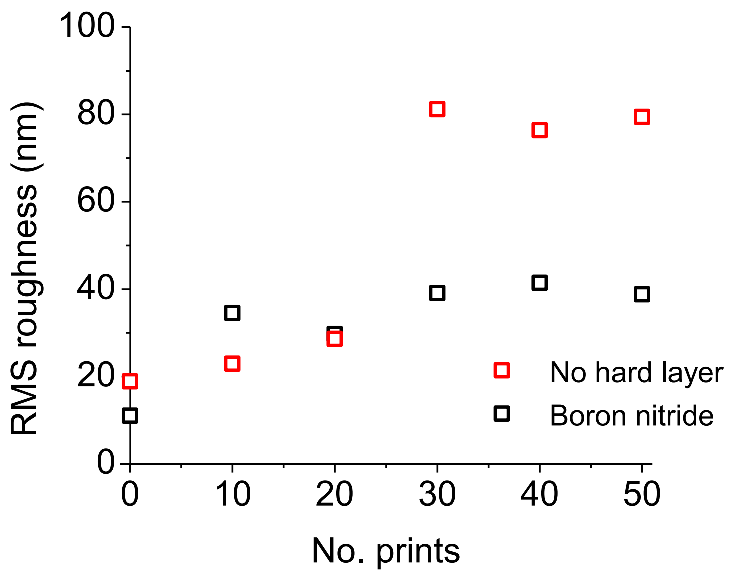


Figure 7. Boron nitride hard layer leads to less roll scratching and lower surface roughness after multiple prints.

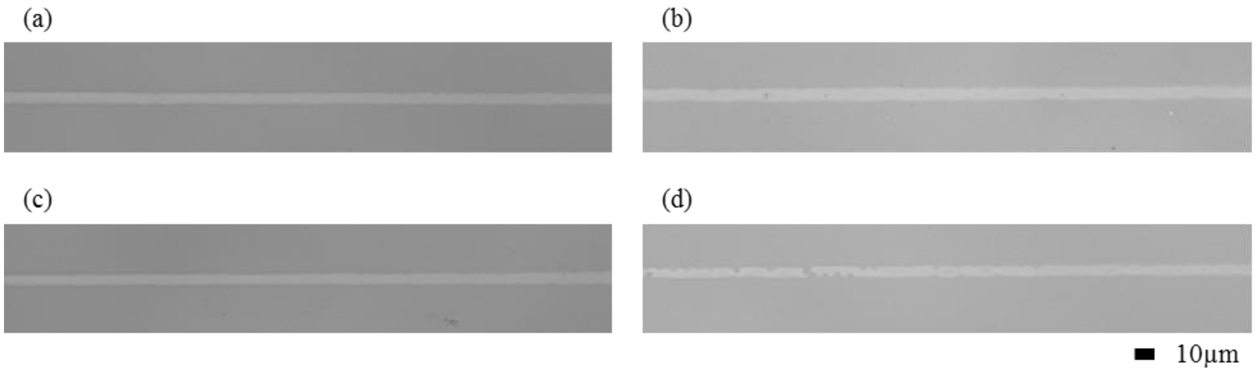


Figure 8. Print quality with scratches after multiple prints. (a) With boron nitride hard layer with new roll. (b) Without boron nitride hard layer with new roll. (c) With boron nitride hard layer after 50 prints. (d) Without boron nitride hard layer after 50 prints. With hard layer print quality does not degrade significantly over 50 prints. Without hard layer lines show breaks after 50 prints.

4. CONCLUSIONS

A novel process to fabricate high-resolution gravure rolls is demonstrated here. With this process gravure rolls are fabricated by replication of a silicon master. Superior control over feature size, surface roughness, cell placement and cell shape is achieved by using standard microfabrication techniques to fabricate the silicon master. These superior properties are transferred to the metal plate that can be mounted on a roll. Printing of 2μm lines at a high speed of 1m/s is demonstrated with this roll. A hard layer is shown to improve both the maximum printing speed at which high-quality features can be printed as well as surface scratching over the course of 50 prints.

5. ACKNOWLEDGEMENTS

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