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Proton beam fabrication of nickel stamps for nanoimprint lithography

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Abstract

Nickel stamps with micro and nano-scale relief features on their surfaces have been fabricated using proton beam writing coupled with nickel sulfamate electroplating. A focused beam of sub-micron 2.0 MeV protons was used to direct-write 3D patterns into spin coated PMMA resist, and a single step nickel sulfamate plating process has been used to produce metallic negatives from these patterns. The fabricated metallic stamps exhibit high aspect ratio surface patterns with smooth and vertical side-walls. Nano-indentation and atomic force microscopy (AFM) measurements of the features on the surface of the stamps indicate a hardness and side-wall roughness of 5 GPa and 7 nm respectively. Using nanoimprint lithography, the stamps fabricated using proton beam writing and electroplating have been successfully used to replicate patterns into PMMA.
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1. Introduction

In the emerging field of nanotechnology, there is an increasing demand for low cost high-throughput technologies with the capability of fabricating structures down to nanometer dimensions. Among various nanofabrication techniques, nanoimprint lithography (NIL) has demonstrated several key achievements such as sub-10 nm high resolution over large areas thus enabling low cost and high throughput [1,2]. Recently NIL has attracted increased levels of attention since it is now being considered as next-generation lithography (NGL) on the International Technology Roadmap for Semiconductors (ITRS 2003) [3], and MITs Technology Review [4] has recently put NIL as one of the 10 emerging technologies likely to change

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the world. NIL, also known as hot embossing [2], is a process which differs from conventional UV lithography and e-beam lithography in that features are transferred on to a substrate using a stamp. The stamp with patterns on its surface is pressed into a polymeric substrate at high temperatures and pressures and then released at low temperatures, leaving behind the patterns in the polymeric substrate. Since the minimum feature size is defined by the pattern on the stamp, the quality of the stamp is an integral feature of imprint technology. High resolution 3D stamps are currently made by e-beam lithography and dry etching, and shallow stamps by e-beam lithography and metal lift off. Li [5] has evaluated the relative hardness of stamps made out of various materials including Si, SiO_2, poly-Si, SiC, silicon nitride and sapphire. Commercial stamps from these materials particularly SiO_2, and poly-Si are now available and different research groups have been using them for NIL research and applications [6]. Taniguchi et al. [7] have presented diamond as a candidate mold for NIL and Schulz and Pfeiffer et al. [8,9] have investigated thermosetting polymeric stamps for nanoimprinting. Nickel stamps fabricated by e-beam lithography and electroplating [10,11], which exhibit high resolution features, increased durability, elasticity and hardness, have been used for industrial applications.

We have developed a new fabrication process based on proton beam writing and nickel electroplating for producing high quality 3D Ni stamps with feature sizes down to and below 100 nm. The stamps exhibit smooth, straight and vertical side-walls, ideal characteristics for imprint lithography. The fabrication process combines the lithographic potential of proton beam writing (PBW) to produce the initial features in PMMA or SU8 resists [12], followed by nickel sulfamate electroplating to transfer these patterns into metallic negative replicas. When MeV protons interact with resist, they scatter and lose energy through nuclear and electronic scattering processes. The dominant energy loss mechanism for MeV protons incident on a low Z material such as polymer resist is electronic scattering. Because of the higher mass of the protons compared with electrons, any scattering of the proton beam due to electronic collisions is negligible and therefore MeV protons penetrate deep into the resist whilst maintaining a straight path. The electronic scattering process generates secondary electrons and this leads to chain scissioning in case of positive resists such as PMMA or cross-linking in case of negative resists such as SU8. Because the secondary electrons have a range of only a few nano meters [12], then proximity effects (effects due to unwanted energetic secondary electrons) are small. These characteristics make proton beam writing a fast single-step 3D direct-write technique for the fabrication of sub-100 nm high aspect ratio structures in resists, with 30 nm resolution (potentially less) and less than 3 nm side-wall roughness [12]. Proton beam writing in combination with electroplating provides a unique technique for the fabrication of high quality 3D metallic stamps and masks.

2. Experimental

A schematic representation of the stamp fabrication process at CIBA using proton beam writing is shown in Fig. 1. This process involves the following steps: (a) Coating a conductive seed layer (Au + Cr) for electroplating + adhesion on to a silicon substrate followed by a spin coated layer of resist e.g. PMMA, and subsequent pattern exposure using proton beam writing. Au and Cu are suitable materials used for seed layers for plating. However, Au has good conductivity and is more resist to subsequent processing steps. Unfortunately, Au has poor adhesion to the Si surface, and therefore we also deposit a thin layer of Cr (typically 20 nm) as an adhesion promoter. The seed layers were deposited consecutively in clean room conditions using either e-beam evaporation or sputtering techniques. (b) Deposition of a second metallization layer (5 nm Ti) onto the exposed top PMMA surface which acts as a seed layer for the base of the stamp, (c) Development of the structures. In general, the basic idea in processes (a)–(c) is to produce electrical isolation between the second metallization layer on top of the resist and the bottom seed layer, necessary to prevent formation of voids inside the plated structures. (d) Electroplating of the structures, plus over-

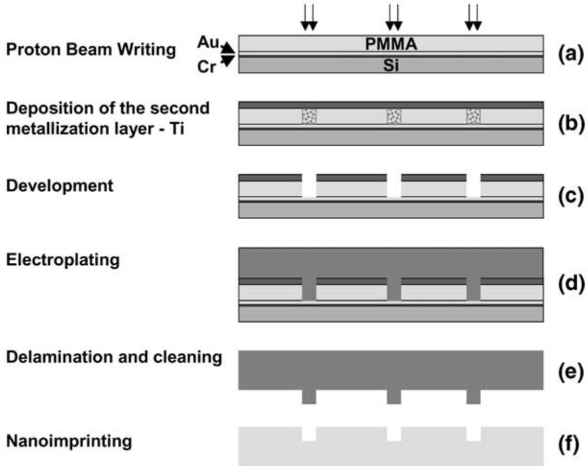

Fig. 1. A schematic representation of the process of stamp fabrication used at CIBA.

plating to form the base of the stamp (an overplating thickness of around 100–300 μm gives the stamp sufficient rigidity for imprinting), (e) Delamination of the stamp from the substrate physically followed by cleaning and (f) final imprinting using hot embossing. A more detailed description of these procedures will be published elsewhere.

The initial lithographic patterning was carried out using the P-beam writing facility at the National University of Singapore [13]. Two kinds of patterned stamps were fabricated in this study. One with micron size features and the other with nanosize features. The patterns can be either elevated features over a large recessed surface (positive relief patterning) or recessed features within a large elevated surface level (negative relief patterning) [14]. In this paper we discuss the fabrication of positive relief stamps.

3. Results

Fig. 2(a) shows an optical micrograph of a positive relief Ni stamp with 20 μm wide and 2 μm high ridges. The initial mold for plating has been written using proton beam writing, and electroplated using a single step process. Fig. 2(b) shows a high magnification scanning electron micrograph (SEM) of one of the ridges which indicates vertical, straight and relatively smooth side-walls. The smoothness of different surfaces of the fabricated stamps (top surface, side-wall and base) was measured using AFM. The top surface of the plated structure indicates a RMS roughness of 2.3 nm, whereas the base surface replicates the smoothness of the second metallization layer on top of the resist and has a RMS roughness of 0.8 nm. The side-wall roughness measured by AFM in tapping mode on the side-walls over an area of $2 \times 2\ \mu m^2$ indicates a value of 7 nm. Nanoindentation measurements were carried out both on the relief features and base of the stamps. A hardness and Young's modulus of 5 GPa and 213 GPa has been measured, which is consistent with previously reported results [15].

For making multiple copies using one stamp, it is important to protect the original stamp from wear and damage. To avoid master stamp deterioration, a metal-on-metal plating process (so called father–mother–son) can be employed [9,10]. This is a process where the original master is plated to create a replicate negative stamp. Fig. 2(c) illustrates the SEM image of this stamp indicating a precise (negative) replication of the master with sharp edges and smooth surfaces. This process is usually only applicable to stamps with low aspect ratio features as high aspect ratio structures face the problem of void formation.

To assess the fabricated stamp performance, we have used our micro-stamps for nanoimprint

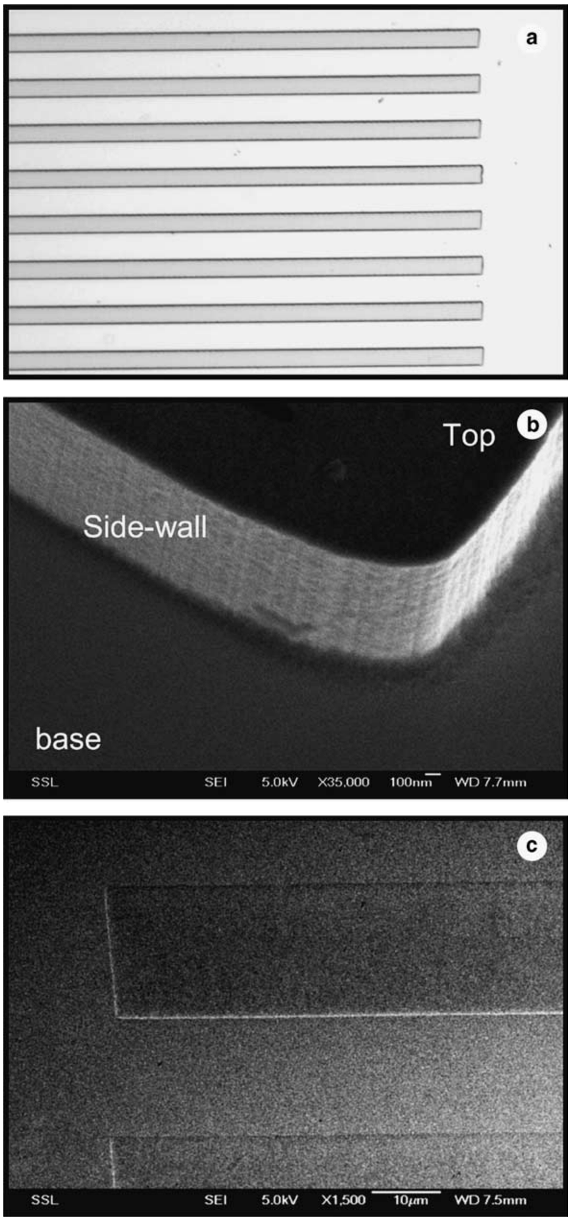

Fig. 2. (a) A low magnification optical micrograph of a nickel microstamp fabricated using proton beam writing and nickel electroplating. The stamp consists of parallel ridges with dimensions of 20 μm (width) × 2 μm (height) × 2 mm (length). (b) An SEM micrograph of the side-walls of the plated ridges of the stamp showing relatively smooth straight vertical side-walls, with smooth top and bottom surfaces, and (c) a high magnification picture of a negative copy of the nickel microstamp fabricated by the process of metal on metal plating.

lithography. The imprint lithography was carried out using a commercial nanoimprinter (Obducat Technologies AB, NIL-2-PL 2.5 inc. nanoimprinter) [16], using hot-embossing lithography. The polymer used for imprinting was a sheet of 2 mm thick PMMA with 3×10^6 g/mol molecular weight. Fig. 3(a) shows an imprinted array of 20 μm grooves and ridges obtained by the stamp shown in Figs. 2(a) and 3(b) shows a high magnification of the imprinted groove imprinted with the same stamp. The replicated patterns indicate high replication accuracy at the micron level, and exhibit smooth vertical straight side-walls with sharp edges, and nearly 90° corners.

The second type of fabricated stamp is again a positive relief type, but this time exhibiting much smaller patterning consisting of narrow ridges of 100 nm, 2 μm high connected to 50×50 μm^2 platforms. The initial patterning of these structures in

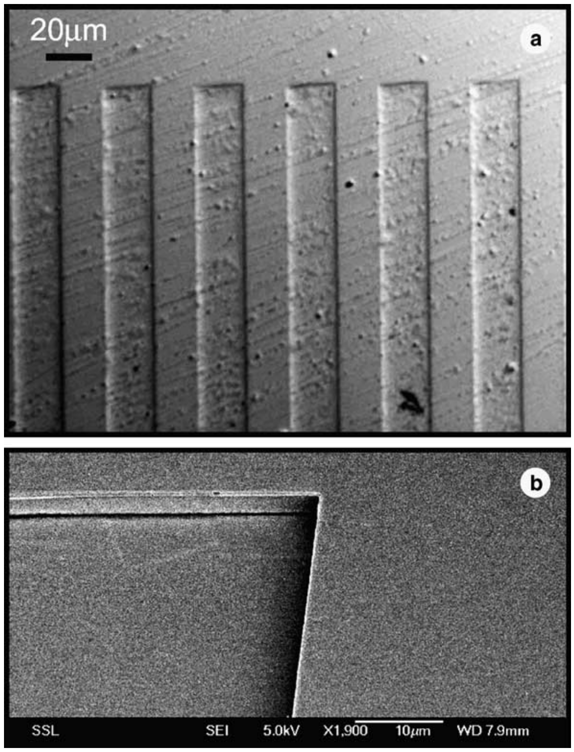

Fig. 3. (a) An optical micrograph of the imprint of the Ni microstamp into bulk solid PMMA sheet. (b) A high magnification SEM image of the imprinted grooves.

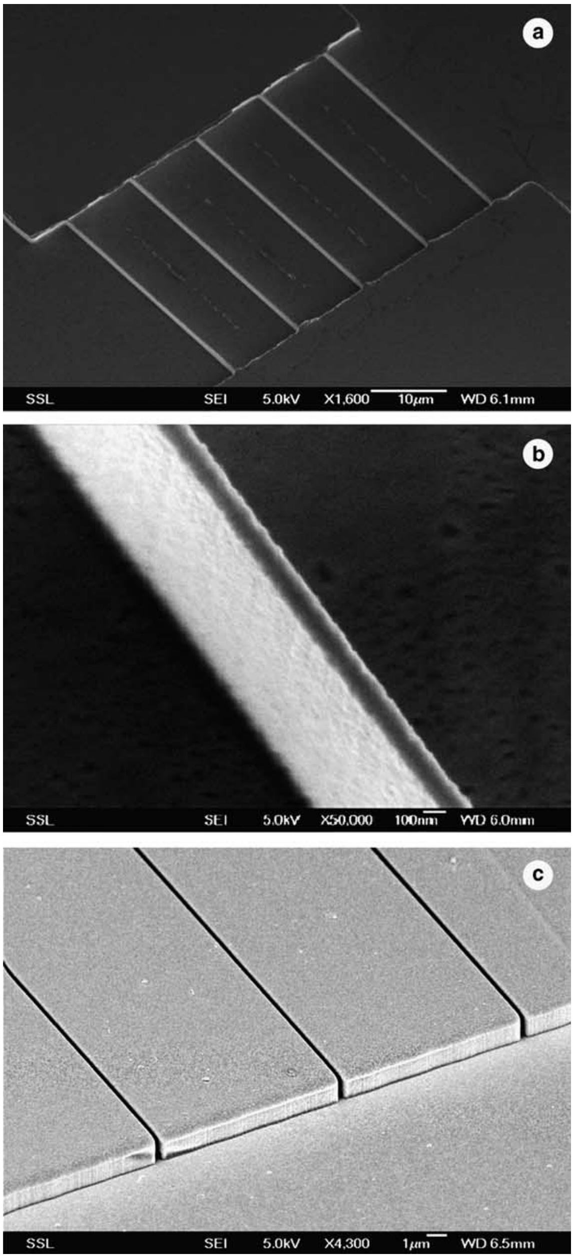

Fig. 4. (a) A low magnification SEM picture of a nickel nanostamp fabricated using proton beam writing and nickel electroplating. The stamp is a test pattern featuring 2 raised platforms connected by five 100 nm wide × 2 μm (depth) × 30 μm (length) high aspect ratio ridges. (b) A high magnification picture of a 100 nm Ni ridge, exhibiting vertical side-walls. (c) An imprint of the above Ni stamp in 8 μm thick PMMA spin-coated on a silicon substrate, showing reproducible fine features, smooth side-walls and vertical structures.

PMMA was carried out using beam of 2 MeV protons focused to a probe size of 60×90 nm^2 with a beam current of less than 0.1 pA. The plating was carried out using a refined technique which avoided voids in the stamp ridges, details of which are given in a previous publication [17]. Fig. 4(a) and (b) show a series of electron microscope photographs, which show the test stamp including the fabricated metallic Ni ridges of 100 nm width and 2 μm height. An electron micrograph of the pattern imprinted into PMMA using nanoimprint lithography is shown in Fig. 4(c). The replicated pattern exhibited vertical straight side-walls and a high degree of replication accuracy, indicating that this process is also suitable for nano-imprinting.

4. Conclusion

We have demonstrated a new way of making metallic stamps utilizing proton beam writing and nickel sulfamate electroplating. Metallic stamps with micron sized features, vertical straight-sided high aspect ratio (~20) walls, 7 nm side-wall roughness, coupled with precise geometry have been made. High-resolution nickel nanostamps with 3D high quality structures featuring 2 μm high, 100 nm 3D patterns with precise geometry have also been fabricated. Both these stamps have been used for imprinting into PMMA with a high degree of replication accuracy. The new technique of imprint lithography has high potential for mass production of components in a wide variety of areas, but requires stamps of precise geometry for its implementation. Here we indicate that proton beam writing has the potential to fabricate high quality stamps down to nanodimensions.

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