Microelectronic Engineering 87 (2010) 1024–1028

Contents lists available at ScienceDirect

Microelectronic Engineering

journal homepage: www.elsevier.com/locate/mee

Study of the behaviour of monomers in thermal nanoimprint lithography

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ARTICLE INFO

Article history:
Received 15 September 2009
Received in revised form 16 November 2009
Accepted 17 November 2009
Available online 14 December 2009

Keywords:
Nanoimprint lithography
Polymer
Monomer
Viscosity

ABSTRACT

Thermoplastics are commonly used in thermal nanoimprint lithography (NIL) but their high viscosity leads to inhomogeneities of residual thickness in patterns with various densities. Monomers exhibit low viscosity and are imprinted easily and polymerized with UV–NIL processes. These monomers can be also used for thermal NIL. We have imprinted A-POSS material which is spontaneously polymerized at 170 °C. The inorganic part of this monomer is interesting for pattern transfer and for permanent applications. Thermal properties of this molecule are presented in this paper. It is shown that polymerization occurs at 170 °C, and that the viscosity is 1330 mPa s at ambient temperature. Imprint experiments have demonstrated that A-POSS flows over larger surfaces during imprint step, compared to thermoplastics. Patterns with different densities have been studied and different filling regimes have been observed depending on material viscosity. They are induced by a competition between material flow and mold deformation. Finally, we imprinted some nanoelectrodes simultaneously with millimetric large connection pads, and it was demonstrated that complete filling was obtained with monomers whereas this was not possible with thermoplastics.

1. Introduction

Nanoimprint lithography (NIL) is very promising for several applications such as nanoelectronics, optics, magnetism, biotechnologies..., and different NIL techniques are now intensively studied [1,2]. Thermal NIL is usually performed using thermoplastics polymers with high viscosity whereas low viscosity monomers are imprinted by UV–NIL. Thermoplastics are commonly used since they were historically used in electronic and optical lithography. Many materials are commercially available and exhibit properties which induce easy use in thermal NIL [3]. But the high viscosity of thermoplastics is one important limitation of thermal NIL since it limits polymer flow over small distances. It has already been shown that flows only occur in mold cavities close to the patterns, and that polymer volume is constant at the period scale [4,5]. It is therefore difficult to print simultaneously nano- and microstructures or nanofeatures with various densities and to achieve a uniform residual thickness (h_r). This limits the use of thermal NIL for applications which requires the transfer of all the patterns into the underneath substrate by etching processes. Main result of the residual thickness nonuniformity is a modification of features dimensions during the transfer step. This is not acceptable for applications using nanostructures, and this issue has been intensively studied. Several solutions were proposed such as adapted mold design [6]. Anisotropic etching processes have been also developed in order to transfer with a high fidelity structures with various densities [7]. But it is nevertheless impossible to print and transfer patterns with too large size or density variation with a guarantee of patterns dimensions. The use of monomers with low viscosity is another solution [8]. In this paper, we present some fundamental studies and imprint results obtained using POSS monomer. Thermal properties of the material have been first studied in order to characterize its behaviour and determine its imprint capabilities. This POSS monomer has been then imprinted using several mold designs. The results presented in last section show the influence of process parameters and an analysis of material flow during the imprint process. Residual thickness has been measured in patterns with various densities printed simultaneously and it is shown how forces, mold deformation and material flow interfere. Finally it is demonstrated that POSS monomer flows on larger surfaces, leading to more uniform h_r. An example of possible application is presented.

2. Experimental

A polysilsesqioxane monomer has been used, and will be named A-POSS in this paper. It has been chosen since it is in a liquid phase at ambient temperature. This parameter is important because it is therefore easier to dilute it in a solvent, compared to powder POSS materials which require often solvents which are not compatible with microelectronics environments. The interest of POSS material

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doi:10.1016/j.mee.2009.11.101

is also its partial inorganic chemical nature, which induce higher stability and higher resistance to plasma etching processes. POSS monomer was diluted in toluene in order to obtain thin films. Depending on the dilution, uniform films were spincoated with a thickness varying from 100 to 350 nm. Thickness was systematically measured by ellipsometry.

Molds have been fabricated by standard DUV lithography combined to plasma etching processes. The mold has been covered with an commonly used Optool antisticking layer. Imprint processes were performed with a EVG®520HE equipment. In standard NIL using thermoplastics, material is heated first to decrease its viscosity, and then pressed to form the patterns. The imprint of monomers is different since viscosity is very small enough to press first the patterns. The force is applied at ambient or limited temperature during 5 min, and monomers are then heated at 170 °C during 5 min in order to achieve polymerization.

All the experiments were performed with 200 mm Si wafers. The entire wafer surface is covered by pattern grating with various feature size and density. The surface of each grating is $5 \times 5\ mm^2$, and they are separated by 1 mm in both *X* and *Y* axes. All the gratings are grouped in one dye, which is reproduced 15 times on the wafer surface. It has been previously shown that imprint process is uniform at the wafer scale, and that results are not impacted by the die position. Several identical patterns were characterized on different dies to improve measurement accuracy. The objective was to demonstrate if POSS monomer exhibits larger flow and an improvement of residual thickness uniformity. Patterns with the highest density variation available on the mold have been therefore characterized. They consist in lines with a 8 μm period. Thinner lines are 1 μm wide and separated by 7 μm, whereas 7 μm imprinted lines are separated only by 1 μm spaces. This results in a density L/S changing from 0.15 to 7. The depth of this mold is 200 nm. The specific characteristic of this mold is that Si surface has not been etched between the pattern areas. The surface surrounding the gratings is therefore pressed into the material. It will be shown in following sections that this has a strong influence on the imprinted patterns. An other mold was fabricated by hybrid lithography combining electron beam and DUV lithography in order to define 100 nm wide nanoelectrodes connected to millimetric pads. The depth of this second mold is 170 nm.

3. Results: properties of material

One important property of NIL materials is their thermal behaviour. In UV–NIL monomers are mixed with a photoinitiator which is activated by UV exposure and initiates monomers crosslinking. It is possible to replace photoinitiator by a thermal initiator which could be activated by heating and lead to same polymerization. But this is not necessary for A-POSS monomer. Differential scanning calorimetry (DSC) and thermal gravimetry analysis (TGA) experiments have been performed in order to characterize thermal properties of the monomers. Result of DSC analysis is presented in Fig. 1a. The evolution of heat flow exhibits an exothermic peak around 160 °C which corresponds to a monomer polymerization. Pure A-POSS monomer was then used for imprinting study. Thermal stability of this material has been characterized by TGA and the resulting graph is shown in Fig. 1b. Material weight decreases rapidly around 320 °C. This demonstrates that A-POSS monomer can be used for thermal NIL with no degradation of the patterns due to possible weight loss. Nevertheless, small decrease between 120 °C and 200 °C should be carefully studied for the use of this monomer for permanent applications. But this has no influence if it is used only as etching mask for pattern transfer. Polymerization which appears around 160 °C has been more precisely characterized by FTIR. Main result is summarized in Fig. 2. It presents the evolution of one characteristic peak as a function of temperature. This peak appears around 1640 cm^{-1} and corresponds to the evolution of a double bond C=C present in the organic part of the molecule. Results of Fig. 2 show that this bond is stable until 150 °C, but completely disappears at 170 °C during molecule polymerization. This demonstrates that imprint processes can be performed at 170 °C and that no higher temperature is required.

Monomers are interesting since their viscosity is very small compared to thermoplastics polymers. This parameter has been quantified, and results are presented in Table 1. It decreases from 1330 mPa s at 35 °C to 615 mPa s at 75 °C. This value is higher than the viscosity of several UV–NIL materials such as Amonil commercialized by AMO GmbH which exhibits a value of 35 mPa s only, but it is comparable to other UV-materials. It has been already demonstrated that residual thickness obtained in UV–NIL is independent on viscosity if it varies from 35 to 1000 mPa s [9], which represents a difference lower than two orders of magnitude. Important difference is between monomer and polymer viscosity. It is known that intrinsic value is higher than 10^4 Pa s. Thin films are used for the duplication of nanostructures by NIL, and standard rheometry techniques are not usable to measure viscosity of such thin films whose properties are influenced by the substrate. Indirect techniques are developed. NEB22 is a resist developed for electron beam lithography, and commercialized by Sumitomo chemicals. Since its glass transition temperature is 80 °C only, and thanks to its polyhydroxystyren nature which leads to high etching resistance, it is already commonly used in thermal NIL. It has been established that the viscosity of NEB22 polymer is

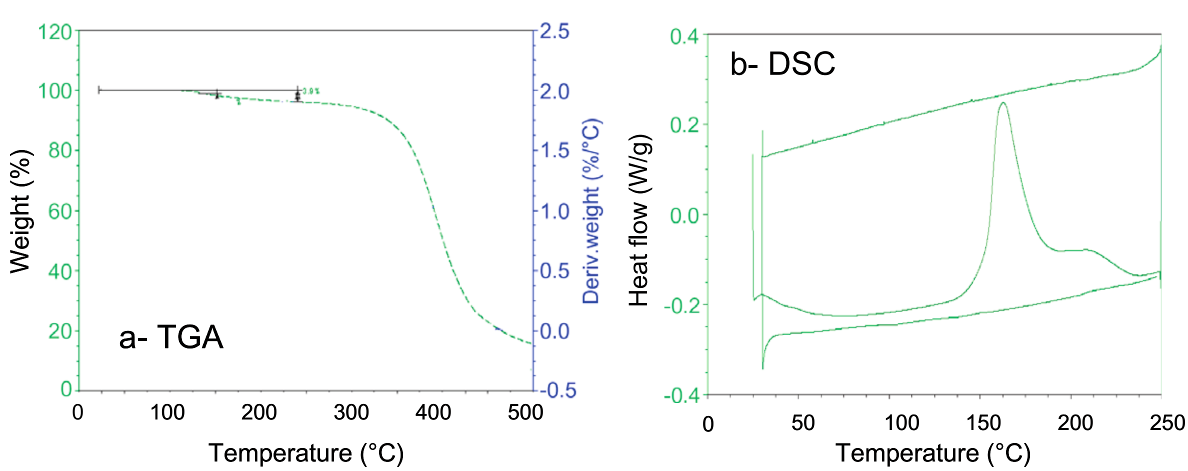

Fig. 1. Weight loss (TGA) and heat flow (DSC) as a function of temperature.