FABRICATION OF MACROPOROUS POLYSILICON BY USING NANOSPHERE LITHOGRAPHY

Chien F. Chau[1], Tracy Melvin[1,2]

[1]School of Electronics and Computer Science/ [2]Opotoelectronics Research Centre, University of Southampton, Highfield, Southampton SO17 1BJ, United Kingdom

cfc03r@ecs.soton.ac.uk

Abstract *— Nanosphere lithography (NSL) has been demonstrated to be a feasible, alternative technique for the fabrication of macroporous polysilicon. The diameter of the pore can be controlled by RIE of the fabricated nanospheres template using Ar/O_2 gas mixtures. The polysilicon can be RIE using $SF_6/O_2/CHF_3$ gas mixtures at pressure of 5mTorr and rf power of 100W.*

Key Words: *Macroporous Polysilicon, Nanosphere Lithography (NSL)*

I INTRODUCTION

Porous silicon has received a great interest since the discovery of its high photoluminescence efficiency almost simultaneously by both Canham [1] and Lehman [2]. Traditionally, the focus has always been on the formation and the application of microporous silicon, which exhibits a pore diameter of <2nm as defined by International Union of Pure and Applied Chemistry (IUPAC) guidelines. Only recently, macroporous silicon, which exhibits pore diameter >50nm, has gained increased attention due to its high aspect ratio structure, in addition to the photoluminescence properties, potentially suitable for the fabrication of photonic crystal [3, 4], anti-reflective coating for solar cells [5], and as sensing material for various applications [6, 7].

Conventionally, periodically ordered macroporous silicon has been fabricated by electrochemical etching using starting pits formed by wet chemical etching [8, 9]. The diameter of the pore thus has a practical limit imposed by optical lithography used to define the initial pits.

Alternatively, nanosphere lithography (NSL) has been well-known as an inexpensive method of producing periodically ordered patterns [10, 11]. NSL technique has been demonstrated to provide masking against ion implantation [12] and electrochemical etching [13] for the fabrication of porous silicon, and serve as the template for the fabrication of nanoholes [14], and nanopillars [15-17]. In the case of macroporous polysilicon, the nanospheres template can be used to define the metal hard mask, which can subsequently be used for the etching of polysilicon.

In this work, we describe the use of such method for the formation of ordered marcoporous structure in polysilicon using fluorine-based reactive ion etching (RIE).

II EXPERIMENT

Carboxylate-modified monodispersed polystyrene nanospheres (Polysciences Europe, Germany) with nominal diameter of 500nm diameter (coefficient of variance of 3%, in 2.65 wt% aqueous suspensions) were used for the experiments. The polystyrene nanospheres were further diluted with De-Ionised (DI) water making into 1% wt suspension. All solvent and chemicals were used without further purification. The major steps in the fabrication of macroporous polysilicon are summarised in Figure 1.

II.1 SUBSTRATE PREPARATION

For the fabrication using NSL, 12mm x 12mm pieces of silicon sample sawn from pre-processed 4 inch silicon wafers were first cleaned by either solvent-based cleaning and/or Piranha clean. The pre-processed silicon wafers consist of 1 μm thick low-pressure chemical vapour deposited (LPCVD) polysilicon (610°C, 10nm/min) isolated from the silicon substrate by a thermally grown (1100°C) 600nm thick silicon dioxide (SiO_2) layer. The polysilicon was doped with either Boron or Phosphorus, and annealed at 1150°C in N_2 for 200min, to achieve a range of sheet resistance from ~28Ω/sq to ~1000Ω/sq.

The solvent-based cleaning uses Acetone, Methanol and DI water sequence, each sonicated for 30min. This process degreases the surface of the substrate. The cleaning method using Piranha mixtures is typically performed using 3:1 volume ratio of concentrated sulfuric acid (H_2SO_4) to 30%

hydrogen peroxide (H_2O_2) for 30min. This cleaning process removes organic and certain metal contaminants, and results in a hydrophilic surface. Piranha mixture is exothermic, which could bring the solution to high temperature and hence should be handled with extreme care.

All cleaned samples were stored in DI water until they were ready to be used to maintain the cleanliness and hydrophilic surface.

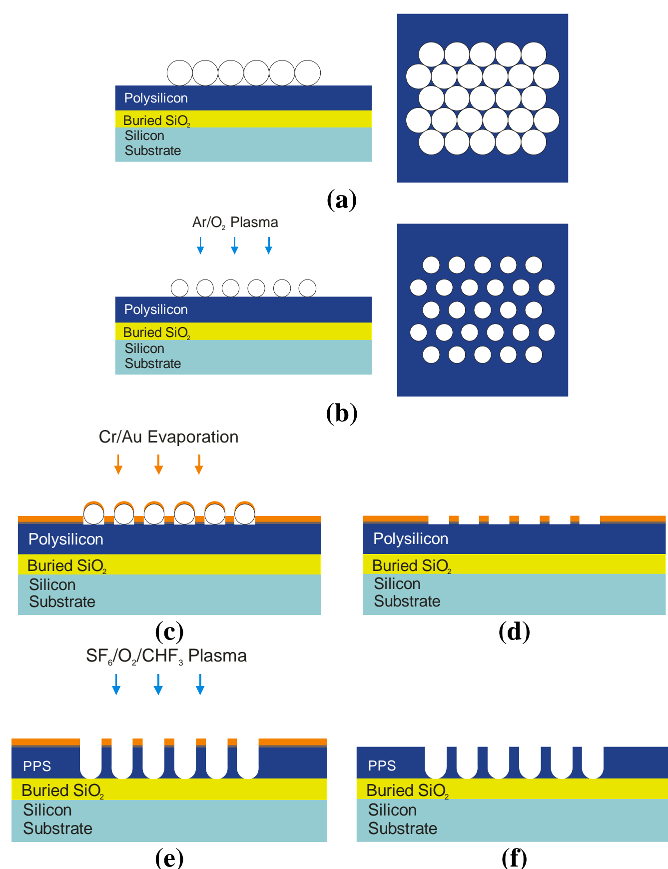

Figure 1. Schematic diagram of the fabrication process of macroporous polysilicon. (a)-(b) Cross-sectional view (left) and top view (right) of process step (a) Deposition of nanospheres template; (b) Size reduction of nanospheres template using RIE with Ar/O_2; (c) Thermal evaporation of Cr/Au metal mask; (d) Removal of nanospheres template; (e) Formation of macroporous polysilicon using RIE with $SF_6/O_2/CHF_3$; and (f) wet chemical etching to remove the Cr/Au metal layer.

II.2 NANOSPHERES TEMPLATE

The self-organised polystyrene nanospheres templates were prepared using a method described by Abdelsalam *et al* [18]. The diluted nanospheres suspension was deposited using an Eppendorf pipette in between a cleaned silicon piece and a thin glass slide, separated by a thin layer of spacer cut from a single sheet of Parafilm. The filled sample was then held vertically in a sealed container to control the evaporation rate. The evaporation process typically takes from 12 to 24 hours. The dried hexagonally close-packed (hcp) nanospheres template has an opal appearance when observed under white light.

In order to create a template suitable for the formation of porous polysilicon, the nanospheres have to be non-closely packed, while still maintaining the hexagonal lattice, as illustrated in Figure 1 (b). This is achievable by reducing the diameter of the nanospheres using plasma RIE. The etching was done in an Oxford Instruments Plasmalab® 80 Plus using a quartz plate. Argon and oxygen (Ar/O_2) mixtures were used (typical gas flow of 5 sccm) at low pressure between 5mTorr and 10mTorr, and a rf power of 100W. The etching time ranges from 2 min to 5 min.

II.3 FABRICATION OF MACROPOROUS POLYSILICON

The size-reduced nanospheres template can then be used as the mask for the subsequent chrome-gold (Cr/Au) metal evaporation and lift-off processes. Typical thickness of thermal evaporated Cr is around 20nm and that of Au is between 60nm and 120nm. The typical evaporation base pressure is 5×10^{-6}mbar using Edwards E306A evaporator.

The metal lift-off is practically carried out by removing the polystyrene nanospheres template using Toluene. This creates a metal mask with periodically ordered holes exposing the polysilicon, as illustrated in Figure 1 (d).

The exposed polysilicon can then be RIE in Plasmalab® 80 Plus using mixtures of Sulfur Hexafluoride (SF_6), O_2 and Trifluoromethane (CHF_3) [19], with gas flow rate of 15, 5 and 6 sccm, respectively. The RIE is carried out at low pressure of 5mTorr and rf power of 100W for 10min. After the RIE, the Cr/Au metal mask can then be removed by using standard gold and chrome etchants.

III RESULTS AND DISCUSSION

III.1 NANOSPHERES TEMPLATE

The nanospheres templates have been successfully deposited onto the silicon pieces. Majority of the nanospheres templates consist of monolayer regions, although there are also areas of multi-layers and isolated clusters of polystyrene nanospheres formed on the samples. At the regions

with monolayer of nanospheres, it appeared to be alternating with densely and sparsely-packed nanospheres, likely due to the uneven evaporation rate. It is also worth noting that the monolayer of polystyrene nanospheres were arranged in a hcp lattice at a densely packed region; while broken clusters of hcp nanospheres appeared at more sparse regions. Figure 2 depicts the scanning electron microscope (SEM) micrograph of a hcp monolayer polystyrene nanospheres template. Due to the naturally grainy surface of polysilicon, some line and dislocation defects could also be observed on the nanospheres template.

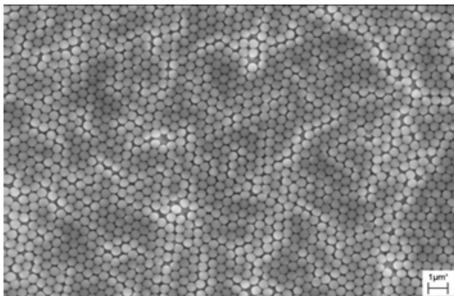

Figure 2. SEM micrograph of a self-assembled nanospheres template formed by 500nm diameter polystyrene nanospheres.

The size of the hcp polystyrene nanospheres has been successfully tuned by controlling the time of RIE using Ar/O_2. By using a 2 min etch at pressure of 10mTorr, the mean diameter of the polystyrene is reduced from the initial 500nm to about 370nm. Due to the nature of the RIE, the surface of the etched polystyrene nanospheres appears rough, similar to observation reported by other groups [14, 15].

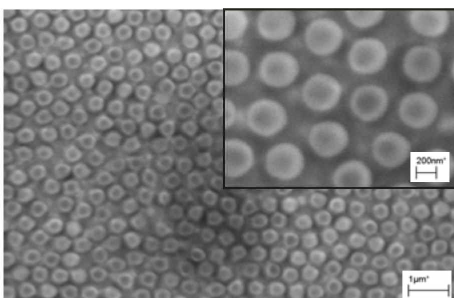

Figure 3. SEM micrograph of a size-reduced nanospheres template after Ar/O_2 RIE of 2 min. Insert: Magnified view of the same sample at different area.

In fact, after a 3 ½ min etch, some of the polystyrene nanospheres appeared to be more elliptical than spherical in shape. SEM micrographs taken on various other samples, such as those depicted in Figure 4 and Figure 5 suggest that the polystyrene nanospheres may have a different material at the outer shell as compared to the inner core. This outer shell swells when subjected to the longer plasma etch time; while the inner core seems to be unaffected by the etching. Further investigation will be carried out to verified this hypothesis.

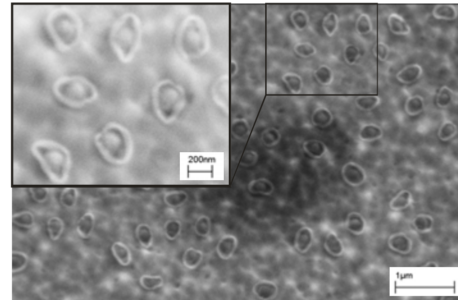

Figure 4. SEM micrograph of a sample undergone a 5 min RIE using Ar/O_2 at pressure of 5mTorr and rf power of 100W. Insert: Magnified view of the top right corner of the micrograph, showing the swelling of the outer shell of the polystyrene nanospheres giving rise to the elliptical appearance.

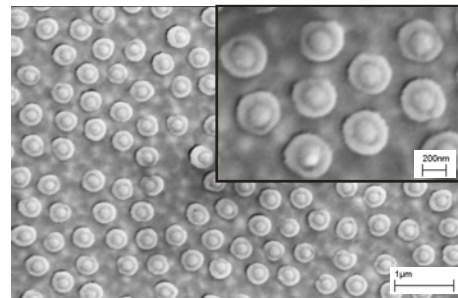

Figure 5. SEM micrograph of a sample undergone a 4 min 15 sec RIE using Ar/O_2 at pressure of 5mTorr and rf power of 100W. The sample has been coated with 17.7nm of Cr and 120nm of Au by thermal evaporation. Insert: Magnified view of the same sample at different area, clearly showing the outer ring and the inner core of the polystyrene nanospheres.

III.2 POROUS POLYSILICON

In order to investigation the feasibility of using Plasmalab® 80 Plus for the RIE of polysilicon using mainly fluorine-based gases, the silicon pieces have been masked by 2μm diameter periodic holes defined by silicon nitride (Si_3N_4) and SiO_2. Both the Si_3N and SiO_2 were fabricated by plasma enhanced (PE) CVD, at 740°C and 400°C, respectively. The periodic holes pattern was prepared by standard optical lithography.

In contrast to the typical Bosch-type deep RIE of silicon, which uses etch and passivation cycles, the

side-wall passivation using fluorine-based RIE is achieved by addition of O_2 into the SF_6 etching [19]. The addition of CHF_3 into SF_6/O_2 gases suppresses the formation of passivation on the top surface, hence smoothens the etched surface. Figure 6 depicts the cross-sectional view of one of the samples undergone a 10 min RIE using this method. The sidewall was relatively vertical with undercut of about 480nm, as compared to etched depth of about 1200nm.

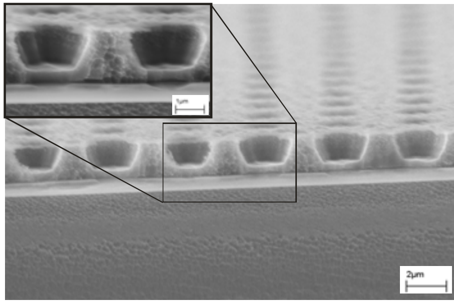

Figure 6. Cross-sectional SEM micrograph of a sample undergone a 10 min RIE using $SF_6/O_2/CHF_3$ at pressure of 5mTorr and rf power of 100W. Insert: Magnified view of the micrograph.

IV SUMMARY

In summary, by using nanosphere lithography, we have described a practical method of fabricating macroporous polysilicon with pore diameter feasibly fine tuned to the respective application. The size of the pore and the pore spacing can be easily controlled by selection of initial diameter of the nanospheres, and further reduced by RIE using Ar/O_2 gas mixtures. We have also demonstrated that by using a gas mixture of $SF_6/O_2/CHF_3$, polysilicon could be RIE with relatively vertical side-wall. Work is currently underway to finalise the fabrication by RIE of polysilicon with metal mask defined by the nanospheres template. The eventual macroporous structure is expected to have wide application in a variety of fields.

V ACKNOWLEDGEMENT

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