Research Article

Fabrication of Metallic Nano Pillar Arrays on Substrate by Sputter Coating and Direct Imprinting Processes

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Abstract
In this study, an efficient fabrication process of metallic nanostructures was proposed and the feasibility of the process was verified. This process comprises of direct imprinting and sputter coating techniques. Firstly in this process, a silicon wafer mother mold of nanopattern is prepared by photolithography and dry etching technique. The nanopatterns of mother mold are transferred to an acrylic film by hot embossing method. Secondly, a quartz glass substrate is cleaned in the acetone bath and then by sputter etching for cleaning the contamination on the surface. Then, a substrate is coated with a gold thin film by the Argon gas sputter coating process. Then, an acrylic film mold, whose surface has been patterned with the nanopatterns, is used to transfer directly of pillar pattern onto the gold thin film. As a result, the gold thin films are inflated as nanopillar arrays on the substrate. This is because of the imprinting load from an acrylic film mold is effective to transfer the nanopillar arrays onto a gold thin film. The experimental results show that an acrylic film mold is effective to form the nanopillar arrays on the Au film although the acrylic film mold is softer than Au thin film. Furthermore, the plasmonic properties of the nanopillar arrays are investigated. It is also found that the plasmonic nanopillar arrays show good performance as a localized surface plasmon resonance (LSPR)-active substrate. Feasibility of the proposed process is confirmed by experimental study, and efficiency of the process is discussed.

Keywords: Direct imprinting, Metallic nanopillar arrays, Sputter coating, Polymer film mold

1 Introduction

In recent years, metallic nanostructures have a great potential to be utilized in various applications in bio-molecular sensors [1], [2], nanoelectronic devices [3], [4], display devices [5], and catalyst [6], [7]. For example, metallic nanoparticles exhibit unique optical characteristics attributed to LSPR (localized surface plasmon resonance), which is due to the collective the oscillation of electrons induced by the electromagnetic field of incident light. The LSPR characteristic is evaluated by absorbance spectrum, where a sharp peak of absorbance spectrum is observed at the wavelength of the resonant frequency. The peak wavelength of the absorbance spectrum is mainly dependent on the size, shape, and alignment of the nanoparticles [8]–[10]. Interestingly, the LSPR resonance frequency is also dependent on the refraction index of the surrounding environmental medium. Utilizing this property, it is expected to be applied to biosensors. Other metallic

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nanostructures such as nanopillars [11]–[13], nanowires [14], [15], nanodots [16]–[18] and nanorods [19] also exhibit unique optical properties due to LSPR, and they are expected to provide excellent performance as LSPR biosensors. Based on these requirements in biosensor application [20], [21], efficient methods to fabricate these nano structures with tunable plasmonic properties are desired.

These kinds of metallic structures of nanometer size are generally fabricated by the conventional nanofabrication processes, such as ultraviolet lithography (UVL) [22] or the electron beam lithography (EBL) [23]. These techniques are useful for production of well-defined and precise metallic structures of nanometer size. However, these processes consist of complicated procedures such as the resist coating, the pattern drawing, etching and developing process, where costly equipment and stringent process control is necessary. In order to develop the high throughput and low cost of a fabrication process, many researchers studied the bottom-up methods such as thermal dewetting [24], [25] and anodic aluminum oxide (AAO) template [26]. These processes are able to fabricate a lot of nanostructures like nanodots and nanoholes by simple procedures. However, it is difficult to control features of nano structures by these self-organization processes.

In order to overcome the previous problems, the authors proposed a new method as a templated direct imprinting method to supplement limitations for the current conventional fabrication methods. In order to fabricate nanostructure arrays of good uniformity and regularity at low cost of fabrication, the authors aim to develop the alternative methods by a PMMA acrylic film mold with groove patterning on the metallic thin film by means of the direct imprinting method. This process consists of three steps; a deposition of the Au thin film on a quartz glass substrate, then patterning of vertical and horizontal groove grid on the Au thin film by the direct imprinting method. A soft acrylic film mold was used to transfer the structure templates on a surface of gold without lithography and chemical etching process. This approach possesses a number of advantages including low-emission, high-throughput, low-cost fabrication techniques, low stringency and without dangerous chemical disposals to destroy the environment are the main issues that need to be addressed.

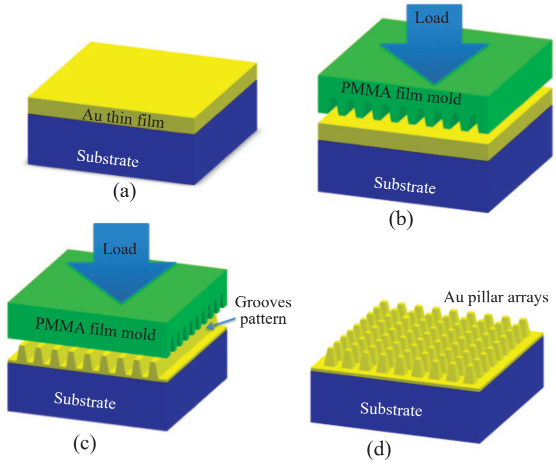

Figure 1: Proposed process for fabrication of the Au nanopillar arrays on substrate.

2 Experimental Methods

2.1 *Experimental procedure for nanopillar arrays fabrication test*

Figure 1 illustrates a newly proposed process for fabrication of an Au nanopillar array on a quartz glass substrate. Figure 1(a) Firstly, a quartz glass plate of 1 mm in thickness was cut into the size of 12×12 mm^2. It was cleaned by an ultrasonic cleaner in an acetone bath for 15 minutes. After the glass substrate was dried in air, Then the glass plate was placed in a DC sputter coater, a substrate was subjected to the sputter etching with Ar gas for 2 minutes to remove the contamination molecules from the surface of a substrate. Then, a gold thin film was deposited on a quartz glass plate for 50 nm in thickness. The spatter gas was Argon (Ar), and its pressure was 15 Pa. The distance between the specimen and the Au target was 35 mm. The thickness of the Au film was controlled by adjusting sputtering time. Figure 1(b) Secondly, the vertical parallel grooves were formed on the deposited Au thin film by direct imprinting method using an acrylic film mold. The acrylic film mold was manually pressed on the surface of the deposited Au thin film using tweezers as shown in Figure 2. A rounded tip with the straight type of tweezers was used in the direct nanoimprinting process. The radius of the round tip was about 1.3 mm. It was made of high-quality stainless steel. Figure 1(c), finally, an acrylic film mold was rotated in a perpendicular

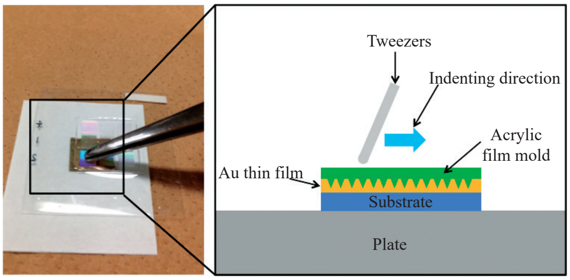

Figure 2: The manually direct imprinting process to transfer the pattern from an acrylic film mold to Au thin film by the tweezers.

direction to transfer the horizontal grooves, Figure 1(d) then the square pillar pattern was agglomerated on the Au thin film on a substrate. Morphology and alignment of nanopillar array were characterized by observation with atomic force microscopy (AFM, Keyence VN-8010).

2.2 *Hot embossing method of a PMMA film mold.*

This study involves the use of parallel groove-shaped as a convenient and easily accessible alternative to nanoscale features fabricated via direct imprinting method. For the mother mold fabrication, the silicon wafer was used as the mother mold materials. The series of parallel grooves were fabricated by photolithography and dry etching techniques. A polymer film mold was fabricated by the following procedure as shown in Figure 3. Figure 3(a) Firstly, the mother mold was imprinted on an acrylic film after heated to 110°C. An acrylic film used in this experiment was poly(methyl methacrylate) film (PMMA), ACRYPLEN-HBA002P. The glass transition temperature of an acrylic film is 105°C. The thickness of the film was 75 µm, the pattern area was 25 mm^2 and the hardness of an acrylic film mold was about 15 HV. Figure 3(b) The mother mold was continuously cooled to room temperature (RT), and the polymer film was peeled off from the mother mold.

The use of an acrylic film mold in the replica molding helps to overcome the damage to the nanostructures on the mother mold. The acrylic film can be removed easily from a mother mold without damaging the nanostructures on either surface during separation process because of the toughness and elasticity property. Moreover, the mother mold can be used for replication to transfer a pattern to the other acrylic film. The acrylic film mold was applied to direct imprinting on the Au thin film coated on a quartz glass substrate.

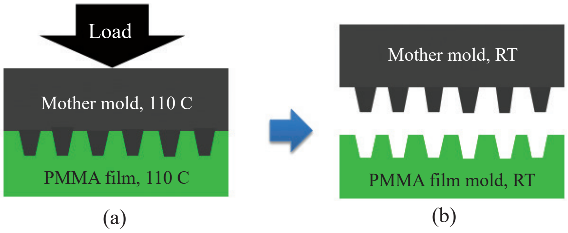

Figure 3: Hot embossing method of a film mold: (a) Mother mold imprint on a PMMA film, (b) Peeling off process.

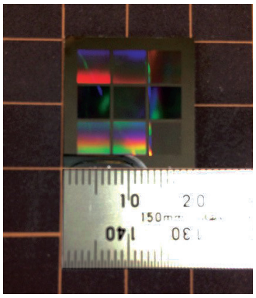

Figure 4: SEM image of a silicon wafer mother mold with the parallel groove patterns.

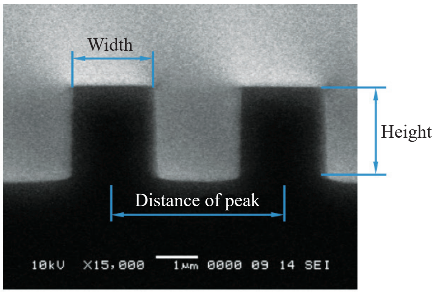

Figure 5: Scanning electron micrographs (SEM) demonstrating the dimension of groove patterns fabricated on the silicon wafer.

In order to fabricate an acrylic film mold, Figure 4 shows the silicon wafer mother mold used for the hot embossing process. The nanostructures were fabricated by the photolithography and dry etching method on the mother mold.

Figure 5 illustrates the SEM micrographs of the vertical cross section for groove patterns on the silicon wafer mother mold. The dimension parameter of each nano-groove patterns are summarized in Table 1.

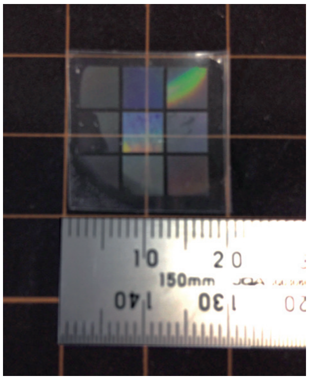

Figure 6: An acrylic film mold with a groove pattern of 5×5 mm^2 for direct imprinting experiment.

Table 1: The dimension parameter of each nano groove patterns on the mother mold

Pattern	Width (μm)	Height (μm)	Distance of Peak (μm)
Grooves	2	3	4

Figure 6 illustrates a photograph of an acrylic film mold. An acrylic film mold was utilized for a direct imprinting test. A groove pattern of 5×5 mm^2 was successfully fabricated from the mother mold onto an acrylic film. Figure 7(a) shows the AFM topography images and Figure 7(b) shows the height profiles along with the x-x' line of the parallel grooves transferred on an acrylic film. The width of crests was 2 μm, the average height of groove was about 1 μm and the pitch of groove pattern was 4 μm, which was nearly the same as the pitch of groove on the mother mold. The fabricated groove structure was analyzed by an atomic force microscopy (AFM, Keyence VN-8010). An acrylic film mold was utilized for a direct imprinting test on Au thin film.

3 Results

3.1 *Metallic pillar arrays on a substrate*

Figure 8 shows the AFM image after the direct imprinting process by using an acrylic film mold. Results have shown that the nanopillar protuberances are regularly aligned onto Au thin film on a substrate. Figure 9(a) illustrates the height profile of the nano protuberances on the horizontal cross-section line as an X-X' and Figure 9(b) illustrates the height profile of the nano protuberances on the vertical cross section line as Y-Y'. A result showed that the distance between pillar is about 4 μm and the average height is about 90 nm. This agrees with the distance of parallel grooves on an acrylic film mold. Thus, it is attributed to plastic deformation caused by an acrylic film mold. According

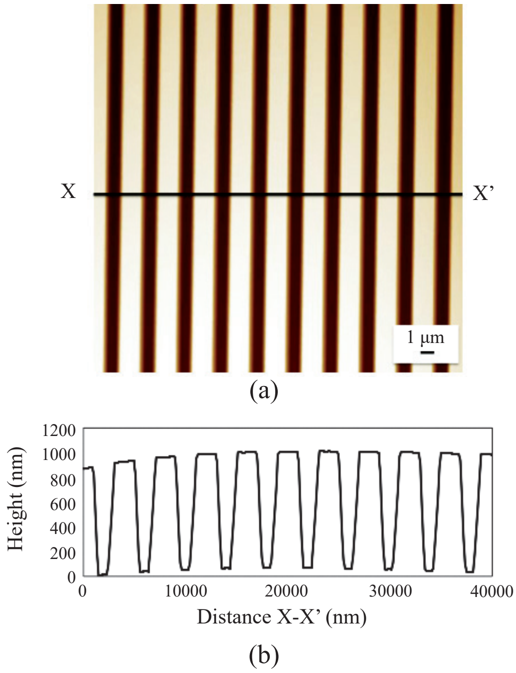

Figure 7: (a) AFM topography image of an acrylic film mold of the width of crests 2 μm parallel grooves pattern and (b) Height distribution along with the x-x' line of parallel groove patterns, the average height of groove was about 1 μm.

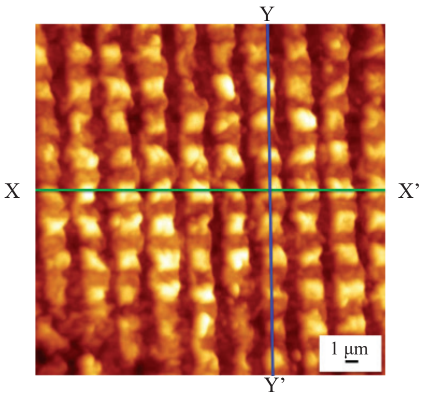

Figure 8: The AFM image of the Au nanopillar arrays on a substarte by direct imprinting process.

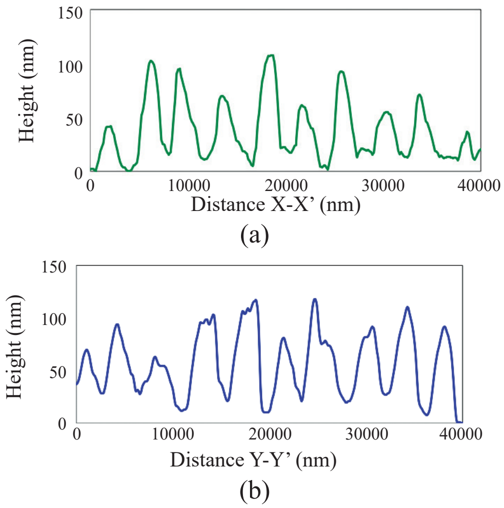

Figure 9: The height profiles of the Au nanopillar arrays on a substrate by direct imprinting process.

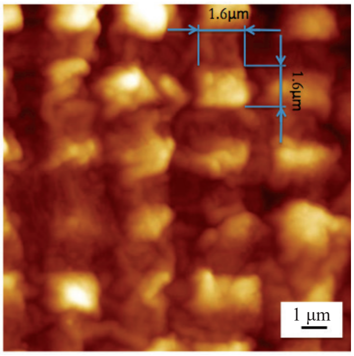

Figure 10: The AFM image of the square area on the top of Au nanopillar arrays on a substrate by direct imprinting process.

to literature, the hardness of Au film is measured at 22 HV [27], which is much higher than the hardness of an acrylic film. Nevertheless, the result shown in Figure 8 indicates that harder gold film was deformed by the softer acrylic film, and an acrylic film mold is effective to fabricate a nanopillar pattern on the gold thin film.

Figure 10 illustrates the dimension of the square area on the top of a gold nanopillar structure. The results revealed that the average square area was 1.6 × 1.6 µm^2. It was also confirmed that a gold film is agglomerated as the square nanopillar structures on the substrate by the direct imprinting method using an acrylic film mold.

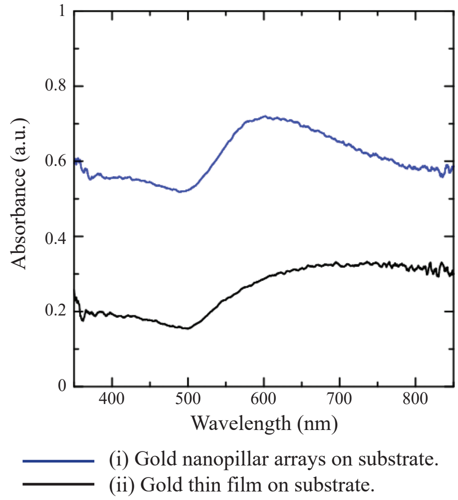

Figure 11: Extinction spectra of gold nanopillar arrays on a substrate fabricated by direct imprinting method.

3.2 *LSPR properties*

To investigate the optical property of the fabricated nanopillars, ultraviolet-visible (UV-vis) extinction spectra were measured by using a spectrometer (BAS SEC2000). The wavelength range of the spectrum was selected over 400–850 nm. Figure 11 illustrates a comparison of the absorbance spectra between (i) the gold nanopillar arrays on the quartz glass substrate fabricated by the direct imprinting process of this study as shown in a blue line with (ii) the gold thin film was directly deposited on the glass substrate as shown in a black line. A result reviewed that, the gold nanopillar arrays fabricated by direct imprinting has an absorbance peak appeared on the wavelength of 680 nm. However, the gold thin film has the spectrum peak appeared on the wavelength of 760 nm. It was confirmed that the absorbance peak depends on the dimension and alignment of nanopillar arrays. The gold nanopillar arrays on substrate exhibit a higher and steeper absorbance peak. It was clearly shown that LSPR property was very sensitive to the pattern of gold nanopillar arrays on a quartz glass substrate.

4 Discussion

In the study, the gold nanoparticles were directly deposited on the surface of a substrate by a sputter coating process. The yield stress of Au nanoparticle is

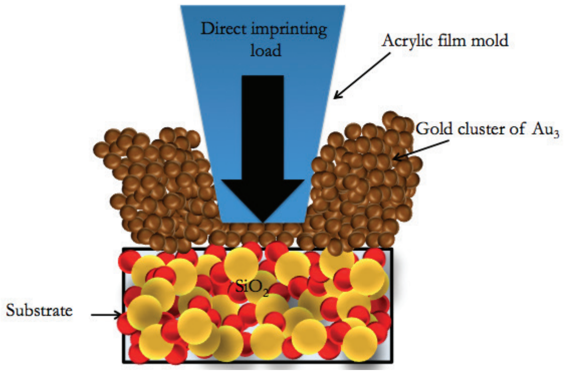

Figure 12: The demonstrating of an indentation behavior of a PMMA acrylic film mold by direct imprinting method onto the Au cluster film deposition on a quartz glass substrate.

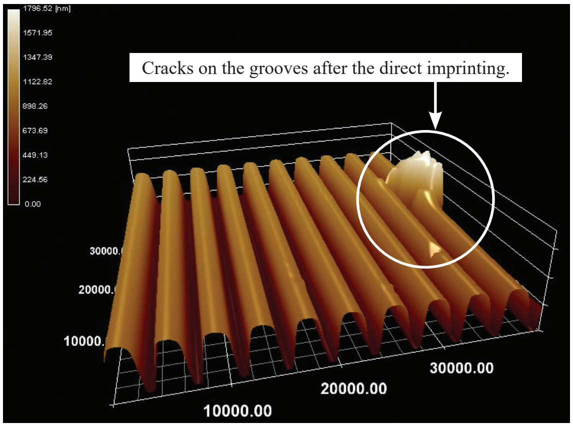

Figure 13: The structured polymer surfaces after the direct imprinting process.

approximately 216 MPa [28], [29]. However, The yield stress of PMMA acrylic film mold is 42 MPa from the product description of PMMA, ACRYPLEN™ HBA002P [30]. The result of this study indicates that the hard gold thin film was deformed by the direct imprinting process. In spite of the yield stress of an acrylic film mold is lower than the gold thin film, the patterns can be transferred by a load of direct imprinting method onto the gold thin film.

One of the reasons for this possible compression mechanism is attributed to voids in the gold coating film. In this study, the height of grooves on an acrylic film mold was about 1 µm (1000 nm). The thickness of gold thin film on a substrate was coated for 50 nm. As shown in Figure 12, the acrylic grooves with the height of 1000 nm were directly pressed onto the 50 nm thickness of coated gold film layer. The gold thin film had a coarse microstructure in which minute grains of gold were piled up like a sand layer. After an acrylic grooves penetrated into the gold thin film at some indentation depth, then some of the gold clusters have flowed over into the cavity of an acrylic grooves. Therefore, the height of gold layer in the cavities were continuously increased throughout the direct imprinting process. However for the cross direct imprinting of this study, it was revealed that the gold pillar structures with the thickness about 90 nm were formed on the glass substrate.

Another possible reason for this phenomenon is the increase of hardness of the PMMA film mold caused by the imprinting pressure. The width of the crests of the mold was 2 µm, whereas the space between crests was 2 µm. The compressive stress concentrates on the crests, and the stress becomes double that of the imprinting pressure. Because of this high compressive stress, the crests would be compressed elastically, and the density of the crests would be increased. Therefore, the hardness of the crests might be increased.

In addition, the alignment accuracy of pillar structures on the gold thin film is also inherently low as shown in Figure 10, because of increased sizes variation of the crests on groove patterns of a PMMA film mold due to the manually imprinting load by the tweezers. Therefore, the development of a uniform direct imprinting technique that can form narrow and dense pillar arrays is necessary to realize the proposed fabrication process of metal nanostructures.

The limitation of this direct imprinting process by a soft material as the acrylic film mold is, in fact, the reusing of mold. As shown in Figure 13, the crests of groove patterns were destroyed after the direct imprinting process by tweezers. Therefore, the drawback of this study is an acrylic film mold cannot use for the replication. The advantage of this process is that it does not require expensive equipment other than a sputter coater and that it does not use hazardous chemicals, such as acid or alkali solutions. The fundamental mechanism of this process is the indentation on metal films by the low cost of materials such as an acrylic film mold. For this purpose, it is necessary to find a polymer material that can achieve a reusable property.

5 Conclusions

A new fabrication process of the square shape nanopillar arrays, which employed the cross-sectional of vertical and horizontal groove patterning by the combination of the sputter coating and direct imprinting method was proposed. A soft acrylic film mold was used instead of a hard mold for direct imprinting to transfer the nanostructures onto a surface of Au thin film. Then direct imprinting of nanopillar arrays on a substrate was investigated experimentally. The results summarized as follows.

The proposed process is effective to produce an ordered Au nanopillar array aligned on a pattern by an acrylic film mold indentation has been developed. The indentation process of the direct imprinting was examined experimentally. A process that employs the scraping on the behind side of a polymer film mold with the tweezers. Even though the coated Au layer on the quartz glass substrate has the hardness (22 HV) greater than the PMMA film mold (15 HV), it can be fabricated by direct imprinting method to transfer the cross-section of vertical and horizontal parallel grooves by a PMMA acrylic film mold on the Au thin film. A result has shown that the gold nanopillar arrays on a quartz glass substrate were fabricated by direct imprinting process with uniformity of square shape. Most important of all, the nanostructures can be fabricated by using a very high throughput process without using any photo-resist layer, lithography, and chemical etching in the process.

The absorbance spectra of the gold nanopillar structures on the quartz glass substrate display a peak in the visible range wavelength. The absorbance peak intensity increased when the nanopillar aligned along with the patterns. It was confirmed that the variation in the LSPR property is closely correlated to the distribution and alignment of nanopillar arrays on the substrate.

Acknowledgments

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