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Fine patterning of ceramic thick layer on aerosol deposition by lift-off process using photoresist

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Abstract Ceramic fine patterning using aerosol deposition (AD) method and lift-off process was reported. Pre-baking conditions and thickness of photoresist layer were selected carefully to minimize the dimensions of the patterned structure. As a result, a pattern width less than 10 μm for 2 μm thick PZT and α-Al_2O_3 AD-deposited layers was obtained on Si substrate at room temperature.

Keywords Fine pattern · Ceramic thick film · Aerosol deposition · Lift-off process · Photoresist

1 Introduction

Integration and fine patterning of electro-ceramic layer are strongly demanded for many kinds of micro devices such as radio frequency passive components, microelectromechanical systems (MEMS) devices and optoelectronic devices. Various etching processes, such as wet etching [1], ion beam etching [2], reactive ion beam etching [3], plasma etching [4], and reactive ion etching (RIE) [5–7], have been studied to define the patterns on ferroelectric materials such as lead zirconium titanate (PZT) and lead lanthanum zirconate titanate thin films. However, fine patterning of ceramic thick layer over 1 μm thickness is not easy because etching ratio of ceramic layer is generally very low even when inductively coupled plasma (ICP)-RIE, known for its high etching rates, is used [8–10]. Moreover, lift-off process, usually used as an alternative to etching processes, is not applicable to make fine pattern of ceramic layers because the deposition of ceramic layer usually requires high temperature treatment to crystallize the deposited layers. Temperatures over 300 °C used for crystallization will burn the resign polymer-based photoresist making very difficult its removal from the substrate.

The aerosol deposition (AD) method is a unique film formation technology that enables dense ceramic layers to be formed at room temperature [11] by collision of fine ceramic powder with a substrate. During the AD, submicron ceramic particles were accelerated by gas flow in the nozzle to a velocity of several hundred meters per second and sprayed onto the substrate under vacuuming condition. An interesting consolidation phenomenon of ceramics by this method has been found. During collision of fine particles and interaction with substrate, these ceramic particles, not only for oxide (Al_2O_3, Y_2O_3, TiO_2, PZT, etc.) materials but also for non-oxide (aluminum nitride, MgB_2, etc.) materials, formed thick, dense and hard ceramic layers at room temperature. No additional heating for solidification of ceramic powder is required. We named this phenomenon "Room Temperature Impact Consolidation" [11]. Same phenomenon for metal fine particles deposition by AD was also observed. This coating method has many advantages, such as high deposition ratio, low process temperature, high adhesion force with a substrate, in comparison with conventional thin film coating technology and ink jet printing technology. Ceramic materials with thickness exceeding 1 μm can be successfully deposited by this method.

The application of the AD method to micro actuators [12], embedded passive components for high frequency

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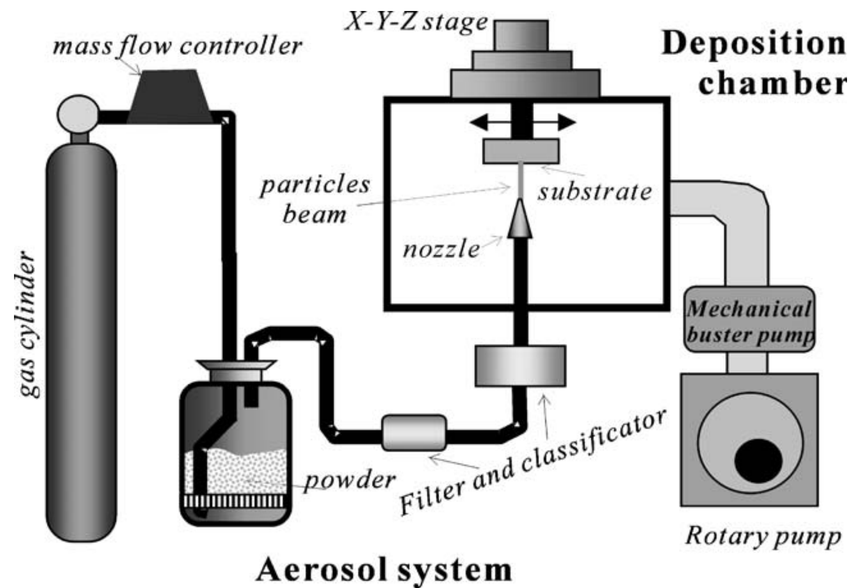

Fig. 1 Basic constitution of the AD apparatus

devises [13, 14], and high speed optical modulators [15] has been already demonstrated.

The patterning of a ceramic layer using stainless steel and polyimide mask has been already reported [16, 17]. It has been reported that patterns with width of minimum 50 µm were successful obtained in this way. However, pattern width less than 50 µm were difficult to obtain. Lift-off process using photoresist for fine patterning of AD ceramic layers has not been reported. In this report, ceramic fine patterning using AD method and lift-off process is described. The hardness and thickness of photoresist layer was chosen carefully. The influence of deposition conditions and post-baking temperature of photoresist materials for pattern profile were investigated.

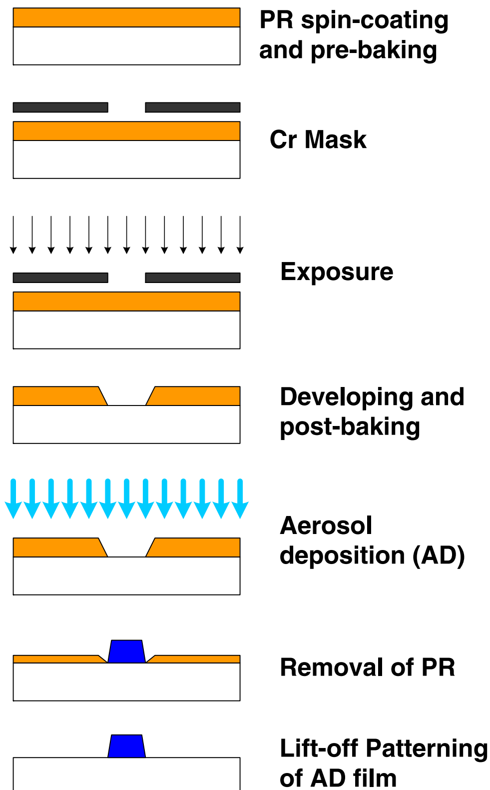

Fig. 2 Flow of Lift-off patterning process of AD ceramic films using patterned photoresist mask

2 Experimental procedure

2.1 Ceramic coating with aerosol deposition method

Figure 1 shows the basic constitution of the aerosol deposition (AD) apparatus. AD machine has two vacuum chambers connected through a gas pipe. One chamber is the deposition chamber for the formation and patterning of films. It contains the nozzle and the substrate and mask alignment systems. This chamber is vacuumed during the deposition by a rotary vacuum pump and a mechanical booster pump. The second is the aerosol chamber for generation of ceramic aerosol. It contains the carrier gas introducing system and vibration system for powder mixing with carrying gas. Fine ceramic powder contained in the aerosol chamber is delivered to the deposition chamber by pressure difference between the two chambers. The ultra fine particle ceramic powder is ejected through the micro orifice nozzle and deposited onto the substrate through masks. Velocities of particles were determined by gas flow

Table 1 Detailed deposition conditions of thick ceramic films with AD method.

Deposition conditions	Thick ceramic films
Powder	PZT and α-Al_2O_3
Substrate	Si wafer and glass
Carrier gas	O_2
Size of nozzle orifice	10×0.5 mm^2 and 20×0.5 mm^2
Scanning rate	1 mm/s
Working pressure	300–800 Pa
Consumption of carrier gas	3–6 L/min
Working distance	10–30 mm
Deposition temperature	room temperature
Deposition area	10×40 mm^2 and 20×40 mm^2
Vibration speed	150–350 rpm

consumption, which was controlled by mass flow controller. During collisions of the fine particles with the substrate, a part of kinetic energy of particles is converted into a bonding energy between the substrate and the fine particles and between the fine particles themselves.

The starting powder used was a commercially available raw-powder material dry-milled and heat treated to improve the deposition rate [18]. According to scanning electron microscopy (SEM) observations, the particle size of the powder varied between 0.08 μm and 1 μm. The size of the particles in the aerosol flow after ejection from the nozzle was between 0.3 μm and 7 μm as measured by an optical scattering method using PCS-2000, PALAS Co. This suggests that partial aggregation of the starting powder particles takes place. In this experiment, to reduce mechanical damage of the ceramic layers and substrate during the deposition, large aggregated particles with a diameter exceeding 2 μm were discarded by an aerodynamic filter.

2.2 Lift-off process for fine ceramic patterning

Photoresist AZ4620 (Clariant Inc.) and LA900 (Tokyo Ohka Kogyo Co., Ltd.) were used as the photoresist masks for fine patterning of electro-ceramic layer. General photoresist lithography processes, spin-coating, pre-baking, setting of Cr mask, exposure and development, were used for the mask fabrication before AD, as shown in Fig. 2. In order to investigate the relation between the mechanical properties and erosion in photoresist induced by collision of the particles jet during AD, the patterned photoresist after development was post-baked at 120, 130, 190 or 230 °C. PZT and α-Al_2O_3 were chosen as the starting powders for the preparation of thick ceramic layers by AD method.

PZT and α-Al_2O_3 films with a thickness of 1~15 μm were directly deposited onto the patterned photoresist by AD method using oxygen as carrier gas at a flowing rate of 3–6 L/min and 2–10 min deposition time. Table 1 shows typical parameters of the deposition condition in AD method. In this work, the distance between nozzle and substrate is longer than that of typical deposition condition in order to reduce the photoresist erosion by ceramic particle jet of AD method. After film deposition, the photoresist was completely removed using acetone for LA 900 and AZ remover 200 for AZ4620.

The mechanical properties of the photoresist and patterned ceramic layers were measured using indentation (Nano-harderness tester, Nanotec Co.) technique. The

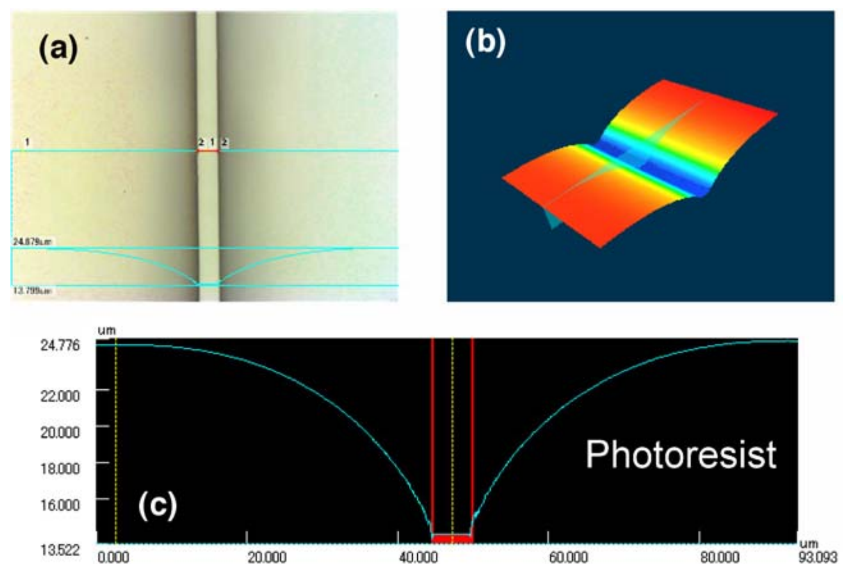

Fig. 3 (**a**) Optical photograph, (**b**) three-dimensional view and (**c**) cross sectional profile of patterned photoresist after development of photoresist and post-annealing of 130 °C for 30 min

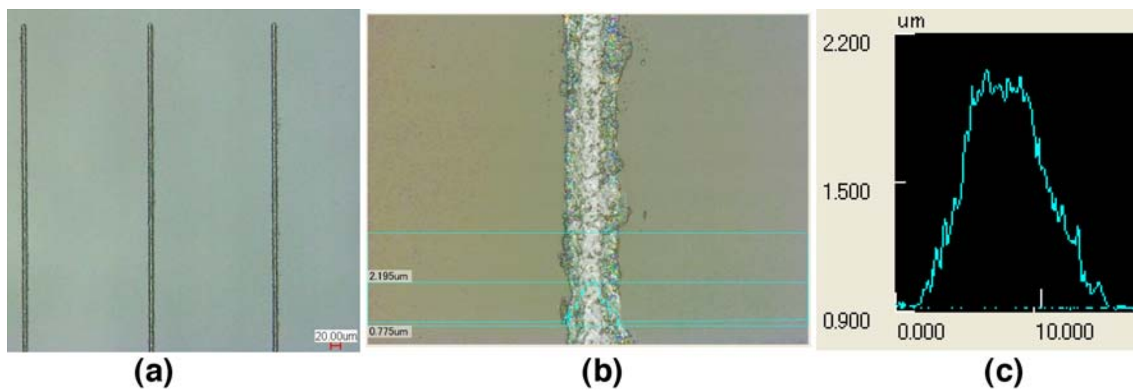

Fig. 4 (**a**) top view photograph, (**b**) its zoom up image and (**c**) cross sectional profile of fine PZT line pattern, which was made by irradiation of PZT particles jet onto the patterned photoresist mask in Fig. 2 with AD method

surface profile and morphology of patterned photoresist and patterned ceramic layer were checked by three-dimensional laser microscopy (VK-9500, KENYENCE). The morphology of ceramic pattern was characterized by (SEM; JSM-5500, JEOL Co.).

3 Results and discussions

Figure 3 shows an optical photograph, a three-dimensional view and a cross sectional profile of patterned photoresist after development and post-annealing at 130 °C for 30 min. The thickness of the photoresist layer after development was approximately 10 μm. The width of patterned line at the bottom (substrate) and top side was 8 μm and about 80 μm, respectively, as shown in Fig. 3(c). The cross sectional profiles of photoresist side wall for patterned edges showed a wide oval shape after post-baking process.

Figure 4(a) and (b) show the top view photograph and its zoom up image of fine PZT line pattern, which was made by aerosol deposition of PZT particles onto the patterned photoresist mask. The deposition time for a 2×4 cm area was 1.5 min. The thickness of PZT line pattern was 1.1 μm. The width of PZT line pattern at the bottom and the top were

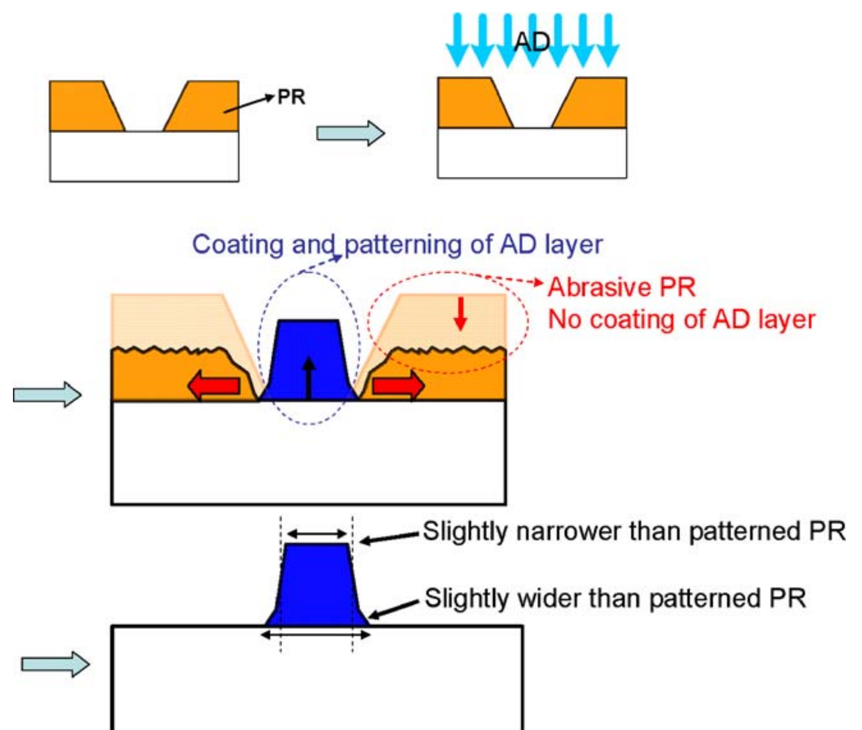

Fig. 5 Schematic of the proposed patterning mechanism of AD ceramic films using the patterned photoresist mask

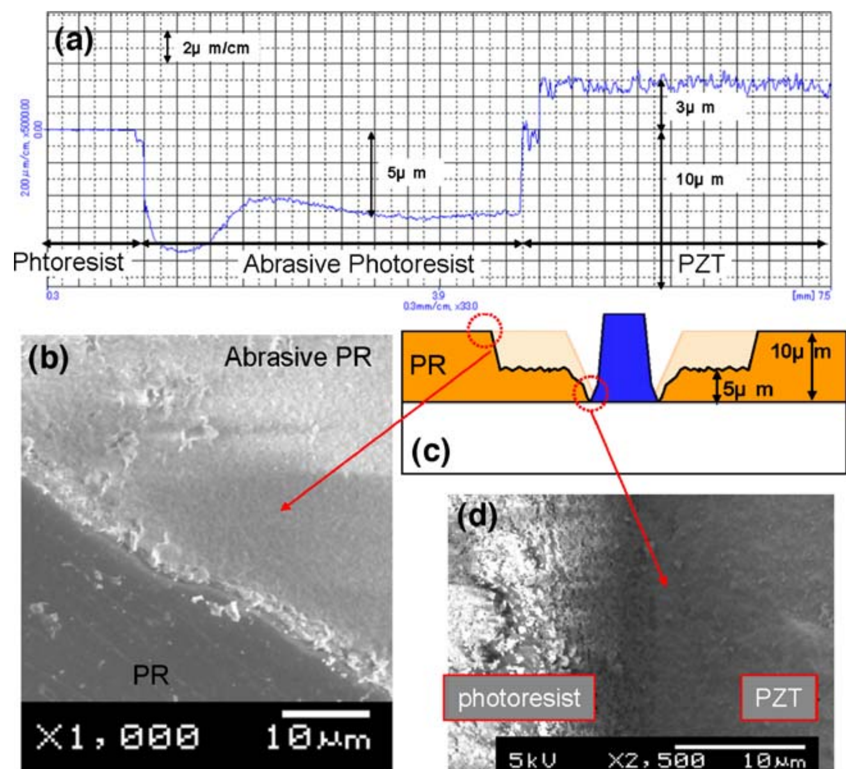

Fig. 6 (**a**) cross sectional profile of photoresist, abrasive photoresist, and thick PZT films before removal of the photoresist., (**b**) top view SEM images of the interface between photoresist and abrasive photoresist by PZT particles jet with AD method, (**c**) its schematic diagram, and (**d**) top view SEM images of the interface between abrasive photoresist and patterned thick PZT films

approximately 15 µm and 5 µm, respectively. The aspect ratio, defined as photoresist etching rate relative to film deposition rate, of the patterned PZT line was 0.073~0.40. The width of the PZT line pattern at the bottom was slightly wider than that of patterned photoresist. The edges of line pattern were not fine, as shown in Fig. 4(b). Figure 4(c) shows the sectional profile of the PZT line pattern. Side walls of the PZT pattern were not steep and have large tails. These poor patterning properties were mainly caused by erosion of photoresist and film side-walls by collision with the particles jet as shown in Fig. 5. During the deposition of PZT layer, the pattern width of photoresist at the bottom increased by erosion. As a result, the width of the PZT line pattern was increased at the bottom. Moreover, the width of PZT line pattern at the top was slightly narrower than that of photoresist pattern at the bottom because of the erosion of side wall of PZT pattern by collision of the particles jet, which was reported in [16–17].

In order to clearly investigate erosion rate of photoresist LA900 (post-annealing at 130 °C for 30 min), thick PZT layer of more than 10 µm thick was deposited directly onto the photoresist with wide line pattern. Figure 6 shows several top view SEM images and cross sectional profile of the abrasive photoresist and the PZT layers before removal of the photoresist. Surface and side wall of the photoresist in sprayed area by PZT particles jet were eroded, as shown in Fig. 6(b). From the cross sectional profile of AD deposition shown in Fig. 6(a), it can be seen that 5 µm thick photoresist layer has been removed during 10 min deposition of a 13 µm thick PZT layer on a 1 cm×1.5 cm area.

The erosion properties of the photoresist must be influenced by its mechanical properties, such as hardness and coefficient of elasticity. To confirm this, patterning properties using several kinds of photoresist materials with different post-baking conditions have been investigated, as shown in Table 2. The hardness of the photoresist slightly increases with increasing of post-baking temperature. On the other hand, the coefficient of elasticity of the photoresists slightly decreases with increasing of post-baking temperature. This means anomaly behavior of indentation process. Figure 7 shows the optical photography of indentation patterns made on photoresist post-baked at different temperatures. Cracks from three corner edges of triangle indentation pattern were only clearly observed in photoresist AZ4620 post-baked at 120 and 190 °C, as shown in Fig. 7(a) and (b). The photoresist AZ4620 post-baked at 120, 190 °C shows a brittle property. Under above conditions, strong erosion of the photoresist was observed by spraying of ceramic particles jet during AD method. On the other hand, these cracks were not observed for photoresist LA900 post-baked at 120 and 130 °C, and photoresist AZ4620 post-baked at 230 °C suggesting that these films have ductile property. Moreover, strong erosion

Table 2 Mechanical properties by different post-baking conditions and several kinds of photoresist.

Photoresist (PR)	Post-baking temp (°C)	Removal of PR	Lift-off patterning by ADM	Hv	Eit
AZ4620	120	○	×	38.842	14.426
	190	△	△	39.280	12.708
	230	×	○	41.664	10.808
LA900	120	○	○	33.635	11.830
	130	○	○	37.380	11.323

○: good, △: not good, ×: bad

of the photoresist was not observed in these cases. These results indicate that ductile property of the photoresist would be a very important factor to reduce the erosion of the photoresist during AD process. At the same time, the photoresist cannot be removed from the substrate if it was post-baked at temperatures over 150 °C by either acetone or special photoresist remover because the photo-resist was burned. From the above investigations, only photoresist LA900 with post-baking at 130 °C shows good performance for fine patterning of ceramic AD layers at this moment.

Using above optimized photoresist process conditions, we formed PZT and α-Al_2O_3 ceramic fine pattern on Si substrate. The deposition time for a 2×4 cm area was 1.5 min. PZT fine line pattern with the thickness of 2 μm and the width of 10 μm and α-Al_2O_3 fine line pattern with the thickness of 1.5 μm and the width of 8.5 μm were obtained as shown in Fig. 8(a). Figure 8(b) shows the cross-sectional SEM image of α-Al_2O_3 ceramic fine pattern, which was made by sampling of focused ion beam etching method. It has dense structure. Hardness of PZT and α-Al_2O_3 ceramic fine pattern were 527±12 and 978±101 Hv for 5 points, which were comparable to that of sintered bulk materials. The aspect ratio of these ceramic fine patterns was 0.20. The patterned PZT thin layer with the thickness of 0.25 μm and the width of 3 μm (aspect ratio, 0.10–0.20) was reported in [9]. This aspect ratio of PZT layer in this report was comparable with that of above reported results. Lift-off patterning of ceramic layers using the photoresist on AD method has great advantages in comparison with etching process for ceramic layers using, for example, an RIE, such as reduction of process steps (time) and damage of ceramic layers on the surface because lift-off process is available. And an expensive etching machine and dangerous gasses do not need also.

4 Conclusion

Fine patterning of AD ceramic layers by lift-off process using the photoresist was reported for the first time. PZT

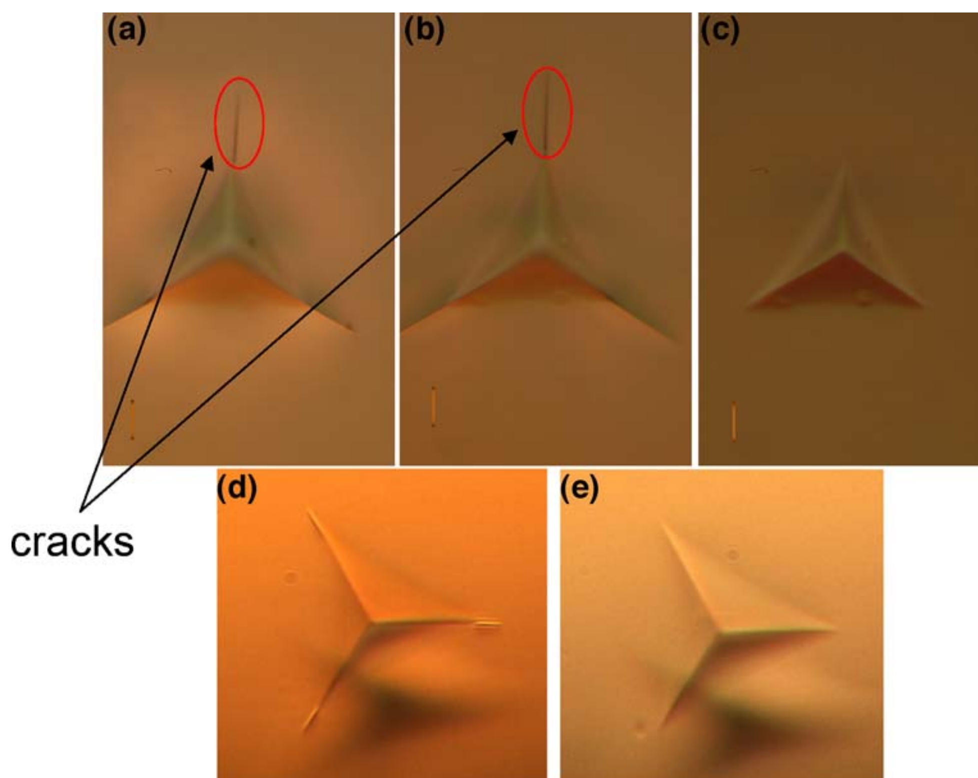

Fig. 7 Optical photography of indentation patterns of the photoresist. (**a**) post-baking 120 °C AZ4620, (**b**) post-baking 190 °C AZ4620, (**c**) post-baking 230 °C AZ4620, (**d**) LA900 at 120 °C, (**e**) LA900 at 130 °C

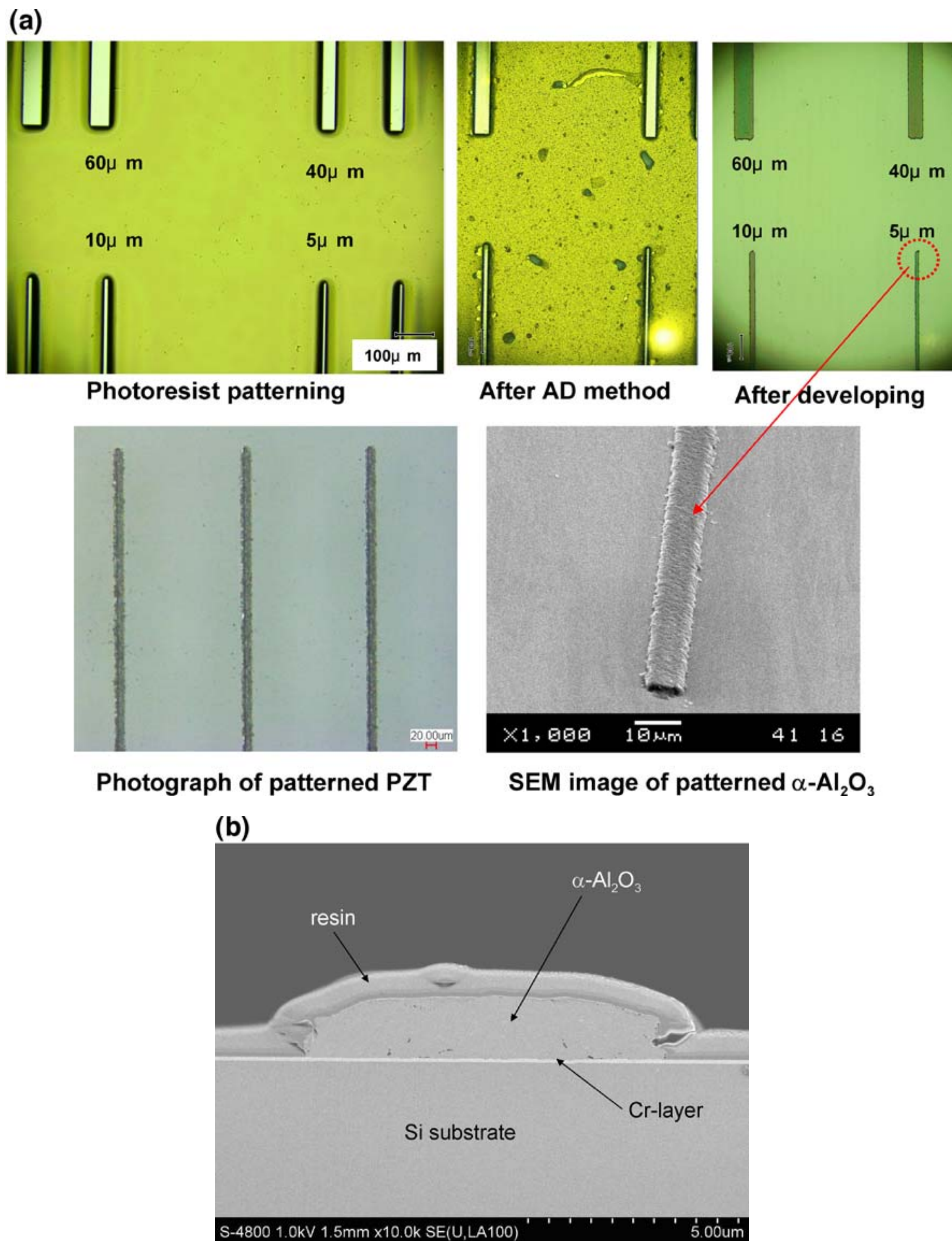

Fig. 8 (**a**) Optical photography of PZT and α-Al_2O_3 ceramic fine pattern on Si substrate. (**b**) Cross-sectional SEM image of α-Al_2O_3 ceramic fine pattern

fine line pattern with the thickness of 2 µm and the width of 10 µm and α-Al_2O_3 fine line pattern with the thickness of 1.5 µm and the width of 8.5 µm were obtained. Formation of crystallized ceramic layer at room temperature as particular characteristics of AD method provides an ability of ceramic fine patterning. Control of the cross sectional profile of patterned photoresist was important to improve the making of fine ceramic pattern. The ductile property of photoresist after post-baking is very important to improve erosion resistance during AD process. More investigations

are needed to unveil the influence of particle diameter of starting powder on AD process for the patterning properties.

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