Patternable Temperature Sensitive Paint using Eu(TTA)$_3$ for the Micro Thermal Imaging

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Abstract. This paper reports a novel patternable temperature sensitive paint (PTSP) which can be photolithographically patterned. The proposed PTSP consists of europium (III) thenoyltrifluoroacetone (Eu(TTA)$_3$) as a luminescent material and SU-8 as a photosensitive matrix. The optimal patterning condition was investigated and the PTSP microstructures as small as 2 $\mu$m were successfully patterned. The luminescence from the micro-patterned PTSP was observed and the temperature sensitivity was measured as high as $0.8\%/^{\circ}\text{C}$.

1. Introduction

Micro thermal imaging is important for the evaluation of a microdevice such as power MEMS and LSI [1]. Because the heat capacity of such microdevices is usually quite small, a non-contact thermal sensing method is required. A far infrared thermography is widely used, but emissivity correction is needed for accurate temperature measurement. In many cases, however, both temperature and emissivity are unknown parameters, and thus precise temperature measurement by thermography is difficult. High speed measurement is often required due to the small thermal time constant. However, thermography using a bolometer is too slow to measure such a high speed phenomenon. In addition, high cost of far infrared optics usually made of Ge is limiting the application field.

A temperature sensitive paint is one of the candidates for high-speed and high-resolution thermal imaging [2–4]. The intensity of luminescence from the TSP is modulated by the temperature, therefore, the temperature distribution can be converted to an optical image. The wavelength of the luminescence is usually in a visible range, and thus a CCD or CMOS imager and a microscope for the visible wavelength can be used for imaging, which can drastically reduce the cost of the system. The lifetime of luminescence is of the order of sub-millisecond [5, 6], which promises a high temporal resolution [3].

Recently, we developed a flash exciting method using a slow-scan CCD camera for high-speed, high resolution and low-cost thermal imaging [4]. The TSP used in the system was manually patterned to open electric contact pads, and the patterning resolution was about a few millimeters. For the temperature measurement of microdevices, however, the micropatterning of the TSP is required. In addition, the micropatterning is essential for a novel low cost thermal imaging device made of TSP, in which the self-suspended TSP microstructures are heated by incident infrared light and their temperature is read out by an optical method [7].
The conventional TSP can be patterned by reactive ion etching (RIE) as shown in Fig. 1. First, the TSP is spin-deposited (Fig. 1 (a)), and then a protective material such as a parylene is deposited on it to protect the TSP from the organic solvent in a photoresist (Fig. 1 (b)). A metal thin film is deposited (Fig. 1 (c)), and the photoresist is patterned on it (Fig. 1 (d)). The metal layer is wet-etched by chemicals (Fig. 1 (e)), and the photoresist is removed. The parylene and TSP are etched by oxygen plasma RIE using the metal layer as an etching mask (Fig. 1 (f)). Finally, the metal layer is removed (Fig. 1 (g)). However, the fabrication process has some disadvantages: The fabrication steps to prepare and remove the etching metal mask are required. The TSP should be protected for the photolithography process, and the plasma process sometimes induces a damage in the TSP. Therefore, we proposed a novel patternable TSP (PTSP), which can be directly patterned by the photolithography technique.

![Figure 1. Patterning process of conventional TSP.](image)

2. Principle of the patterning
The TSP consists of a luminescent material and a matrix. We chose europium (III) thenoyltrifluoroacetone (Eu(TTA)_3) as a luminescent material because of its high temperature sensitivity [5]. Eu(TTA)_3 is dispersed in the matrix (i.e. polymer) to make a film structure. The matrix should be transparent for both excitation UV light (350 nm) and luminescence (610 nm). Polymethylmethacrylate (PMMA) or polyvinylbutyral (PVB) are widely used as the matrix due to their high transparency in a region between near UV and visible wavelength [8, 9]. However, these materials cannot be applicable as the matrix of the PTSP, because they have no photosensitivity. Therefore, we chose SU-8 as the matrix, of which the transparency in near UV and visible wavelength region is excellent [10]. In addition, the protective layer as mentioned in the previous section is not needed due to the high chemical resistivity of SU-8.

Figure 2 illustrates the patterning principle of the PTSP. First, 0.03 mg of Eu(TTA)_3 (Thermo Fisher Scientific Inc., USA) was mixed with 1.0 mL of SU-8 (SU-8 2000.5, MicroChem Corp., USA) to make a PTSP solution. The prepared PTSP solution was spun-deposited on a substrate, baked at 95°C for 1 minute to vaporize the solvent (Fig. 2 (a)), and then exposed to UV light through a photomask (Fig. 2 (b)). Subsequent post exposure baking (PEB) at 95°C activated a cross-linking reaction in the exposed parts (Fig. 2 (c)). Finally, unexposed SU-8 was removed by the developer (Fig. 2 (d)). Eu(TTA)_3 in the unexposed SU-8 was also removed by the developer, while that in the exposed area remained in the SU-8 film.
3. Patterning conditions
The wavelength used for photolithography was 365 nm, which is close to that of Eu(TTA)₃ excitation (350 nm). Therefore, the exposure dose should be higher than that of the normal SU-8 process. In addition, the PEB condition should be also modified, because the cross-linking reaction is inhibited by Eu(TTA)₃. These two parameters are critical for successful patterning and need to be optimized. Table 1 shows the experimental conditions for the photolithography of the PTSP. The exposure dose and the PEB time were chosen as variables, while the other parameters were fixed. Figure 3 shows the patterning results on a Si substrate, where the open circles and crosses show successful and failure conditions, respectively. When the PEB time was short, all patterns disappeared during development (Region (A) in Fig. 3). On the other hand, PEB time longer than about 15 minutes made the unexposed part insoluble in the developer (Region (B) in Fig. 3). Only when the exposure dose was higher than 2400 mJ/cm², there was a process window within PEB time between 5 and 15 minutes (Region (C) in Fig. 3).

Using the obtained process parameters, PTSP micro structures as small as 2 µm were successfully patterned as shown in Fig. 4. The film thickness of the PTSP was about 300 nm.

| Procedure               | Condition          | (Normal SU-8 condition) |
|-------------------------|--------------------|-------------------------|
| Spincoating             | 3000 rpm 30 s      | (3000 rpm 30 s)         |
| Soft baking             | 95°C 1 min         | (95°C 1 min)            |
| Exposure Dose           | 800 ~ 4000 mJ/cm²  | (60 mJ/cm²)            |
| Post exposure baking    | 95°C 5 ~ 32 min    | (95°C 1 min)            |

4. Luminescence property measurement
Figure 5 shows an experimental setup for measuring luminescence from the PTSP at different temperatures. The PTSP was patterned on a Si substrate, and placed on a hot plate with a device holder. The temperature of the substrate was measured by a thermocouple clamped together with the substrate. The PTSP was excited by a UV-LED (SSL-LXTO46355C, Lumex Inc., USA), and luminescence from the PTSP was captured by a cooled CCD camera (BU-50LN, Bitran Corp., Japan) through an optical filter to eliminate the excitation UV light. Figure 6 shows the captured luminescent image, where only the
patterned area are bright due to the luminescence. Figure 7 shows the measured temperature dependency of the luminescence from the PTSP. The intensity is normalized to 1.0 at a room temperature. The intensity reduced with increasing the temperature, which is known as a thermal quenching [11]. The temperature coefficient of intensity (TCI) was measured as high as $0.8\%/{^\circ}\text{C}$, which was smaller than the previous reported values for the normal TSP ($-1.2 \sim -2.0\%/{^\circ}\text{C}$) [4, 5].

![Figure 3. Process window of PTSP patterning. Open circles and crosses show successful and failure conditions, respectively.](image)

![Figure 4. SEM of the patterned PTSP. Exposure dose and PEB time were 2400 mJ/cm$^2$ and 15 minutes, respectively](image)

![Figure 5. Experimental setup for characterizing the PTSP.](image)

![Figure 6. Captured luminescent image of the array of patterned PTSP shown in the inset SEM.](image)
5. Conclusion
We developed a patternable temperature sensitive paint (PTSP) using Eu(TTA)$_3$ and SU-8 as a luminescent material and a photosensitive matrix, respectively. The optimal patterning conditions were investigated, and the maximum resolution as small as 2 μm was demonstrated. The temperature sensitivity was measured as high as −0.8%/°C. Using this technique, various microstructures of the TSP can be easily fabricated without plasma damage. Thus, the proposed PTSP can be applicable for a wide variety of micro thermal imaging applications.

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