

## Electronic Supplementary Information

# Flexible humidity sensors composed of graphite-like carbon micro-pinecone arrays

Tomohiko Nakajima,\* Takako Nakamura and Tetsuo Tsuchiya

Advanced Coating Technology Research Center, National Institute of Advanced Industrial Science and Technology, Tsukuba Central 5, 1-1-1 Higashi, Tsukuba, Ibaraki 305-8565, Japan.

Temperature variations during laser irradiation can be described by the heat diffusion equation simplified to describe one-dimensional heat flow:<sup>1</sup>

$$\rho C \frac{\partial T}{\partial t} = \kappa \frac{\partial^2 T}{\partial z^2} + \alpha I(z, t)$$

where  $T$  is the temperature function at time  $t$  and depth  $z$ ,  $\rho$  is the mass density,  $C$  is the specific heat capacity,  $\alpha$  is the optical absorption coefficient,  $\kappa$  is the thermal conductivity, and  $I(z, t)$  is the laser power density. The laser power  $I(z, t)$  is given by:

$$I(z, t) = I_0(t) \cdot (1 - r) \cdot \exp(-\alpha z)$$

where  $r$  is the reflectance. The contribution from the incremental absorbance of the films caused by reflectance at the substrate surface was also included in the laser power distribution.  $I_0(t)$  is described as a smooth pulse approximated by:

$$I_0(t) = I_0 \cdot \left(\frac{t}{\tau}\right)^\beta \cdot \exp\left(\beta\left(1 - \frac{t}{\tau}\right)\right)$$

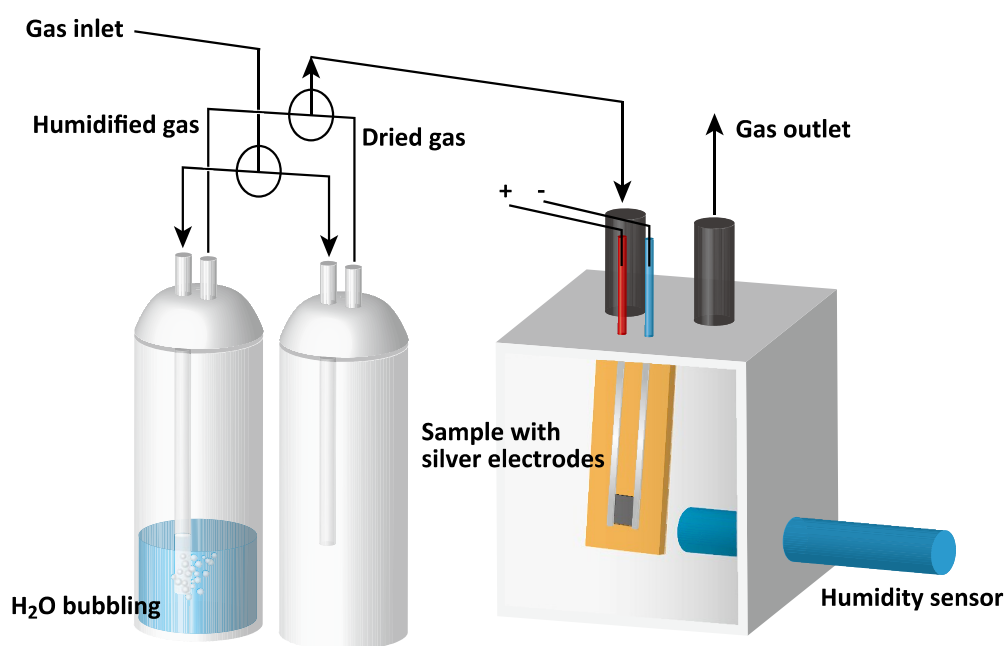
where  $I_0$  is the incident pulse power density,  $\tau$  is the pulse duration (KrF: 26 ns), and  $\beta$  determines the temporal pulse shape (KrF: 6.0). We carried out numerical simulations for the temperature variation for the excimer laser irradiation process using a difference approximation based on the above equations. The initial conditions were  $T = 25$  °C at  $t = 0$  s and  $T = 25$  °C at the bottom of the substrate. The boundary condition was

$\kappa \frac{\partial T}{\partial z} = 0$  at the interfaces. The physical constants used in the calculations are listed in Table S1.

**Table S1** Physical properties used in numerical simulations.<sup>2-4</sup>

Material	$\alpha / \text{cm}^{-1}$	$r$	$\kappa / \text{Wcm}^{-1}\text{K}^{-1}$	$\rho / \text{g cm}^{-3}$	$C / \text{Jg}^{-1}\text{K}^{-1}$
Polyimide	$2.6 \times 10^5$	0.09	$1.2 \times 10^{-3}$	1.42	1.09
Graphite	$1.776 \times 10^4$	0.0377	1.124	2.26	0.72
SiO <sub>2</sub>	0.83	0.08	0.015	2.20	0.67

Figure S2 shows the monitoring setup for the humidity sensing property under various gas flow: humidified/dried N<sub>2</sub>, O<sub>2</sub> and H<sub>2</sub>/Ar. The humidity source was made from water bubbling.



**Fig. S1:** The monitoring setup for the humidity sensing property.

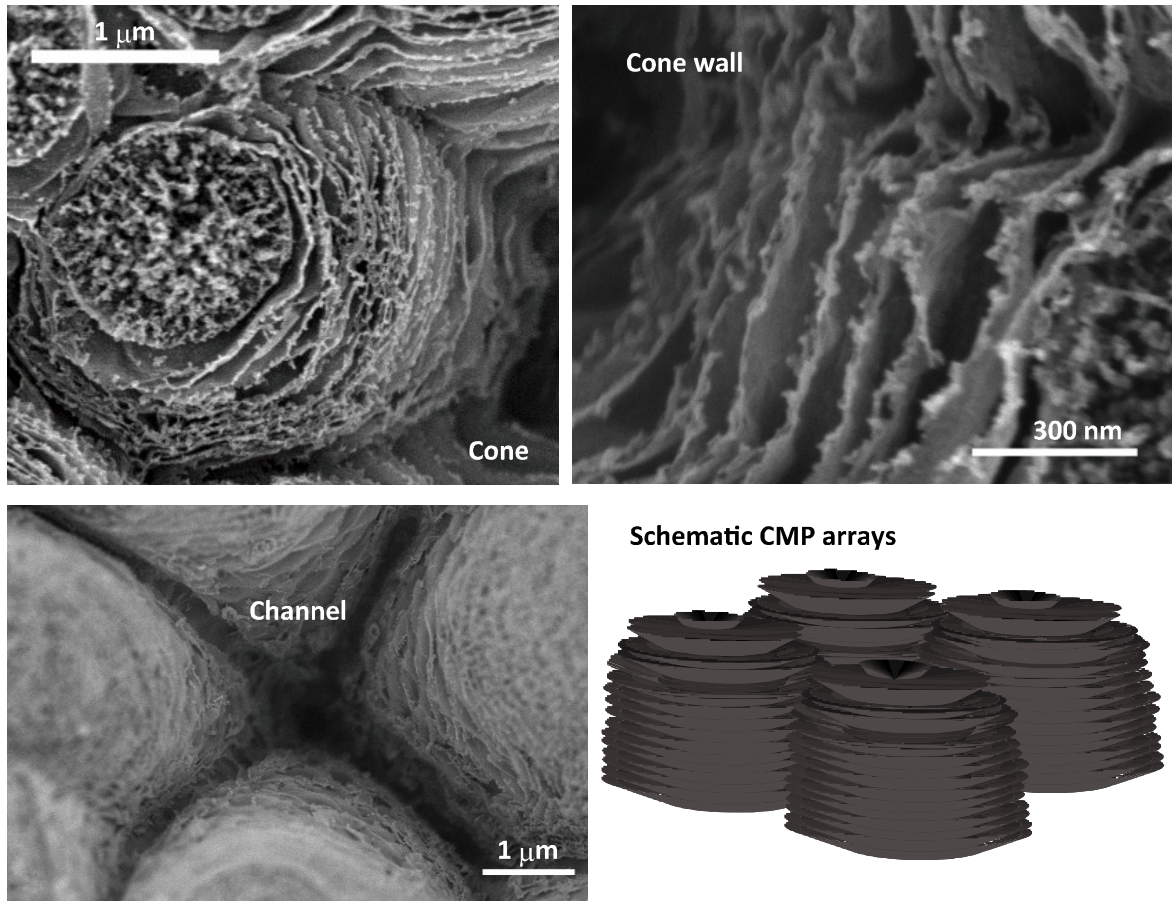


Fig. S2: The FESEM images for the CMP arrays prepared at  $200 \text{ mJ}\cdot\text{cm}^{-2}$  and schematic illustration of CMP arrays.

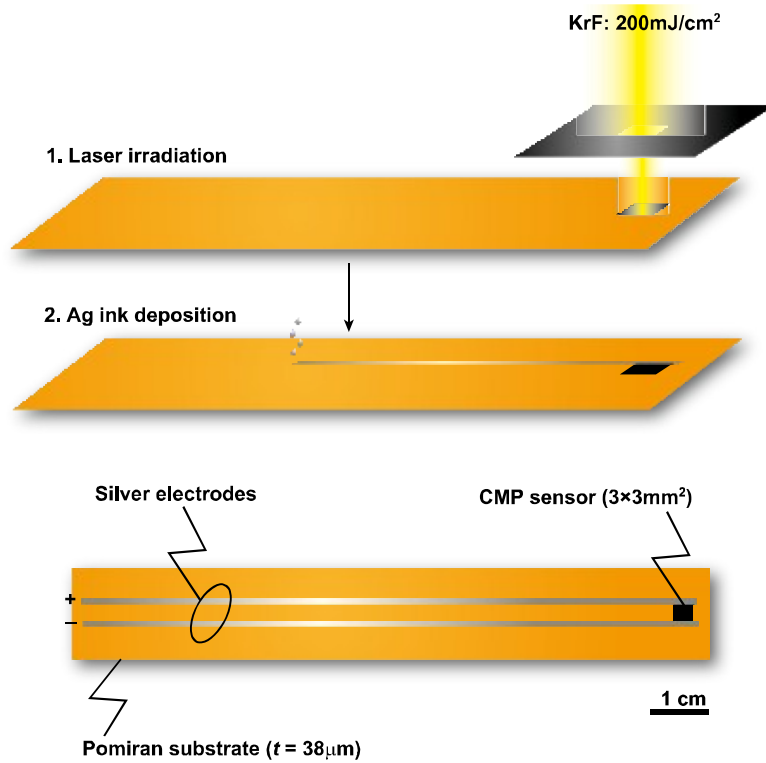
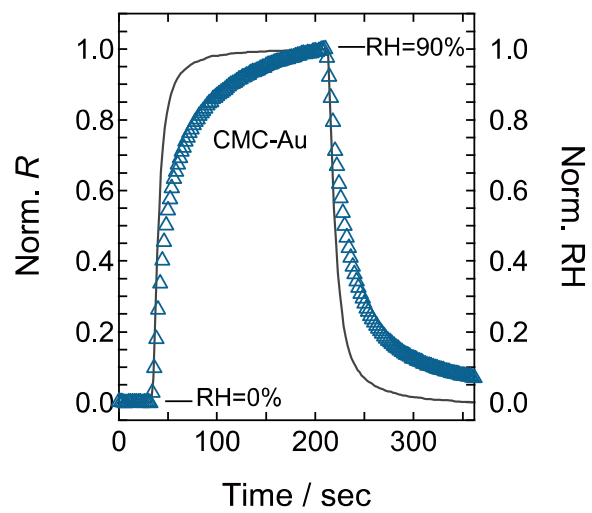
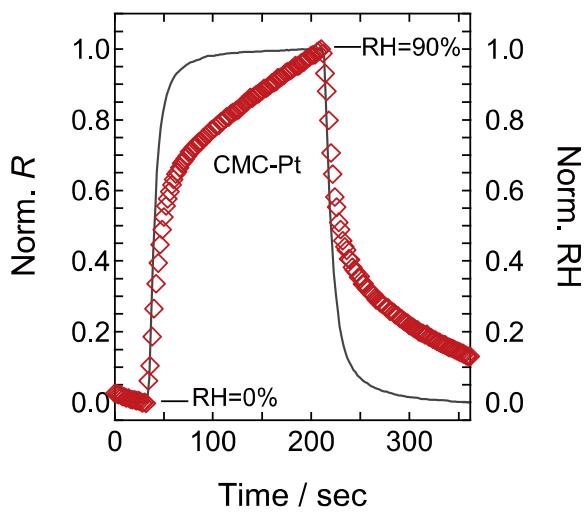
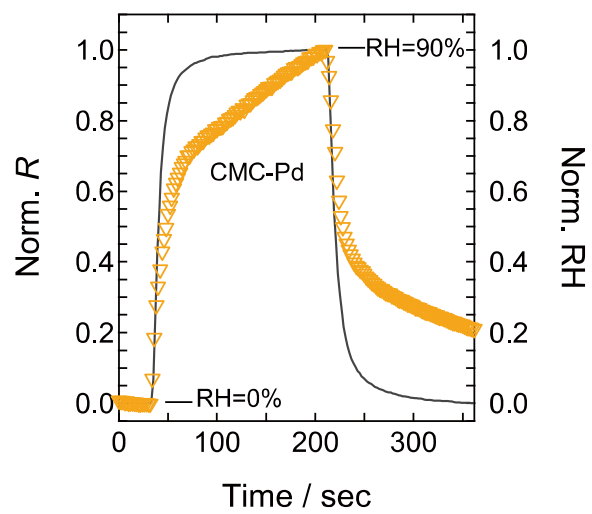
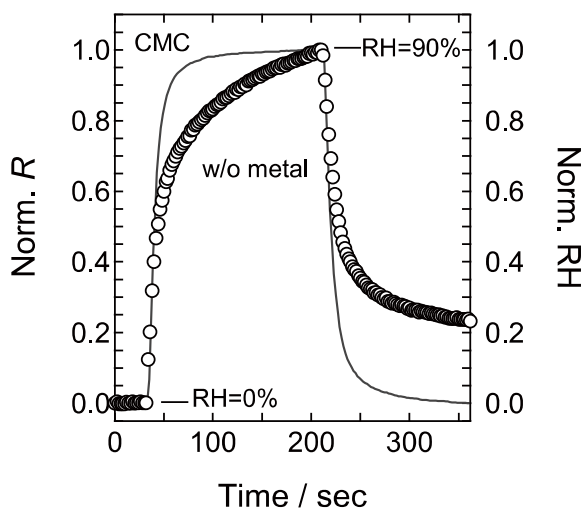
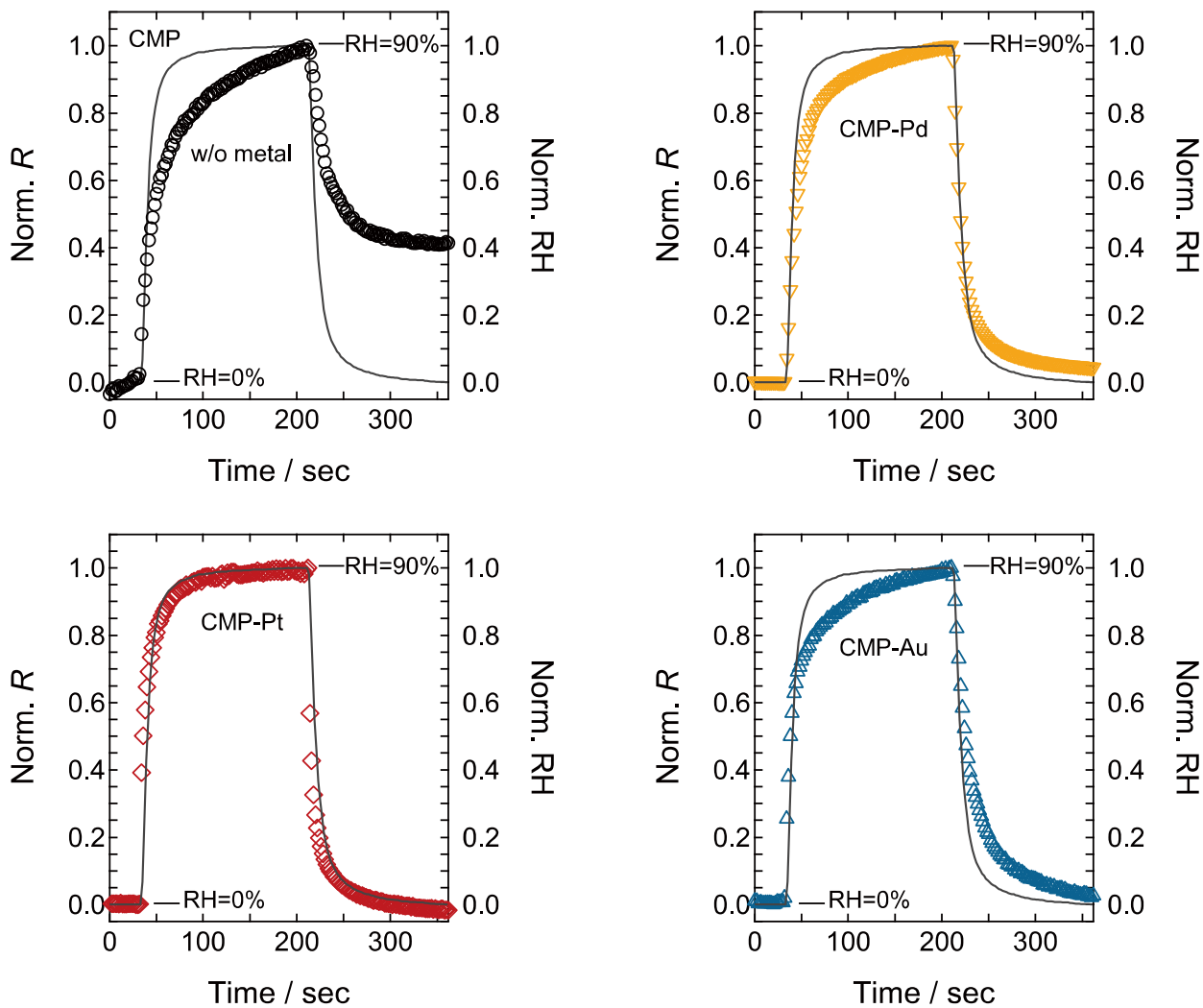


Fig. S3: Schematic illustrations for the preparation procedure and size of the CMP array humidity sensor.



**Fig. S4:** The time course of normalized  $R$  for CMC and CMC-M (M: Pd, Pt and Au). The dotted line represents normalized RH curve monitored by commercial humidity sensor. In the time course measurements, the gas flow was changed as follows: dried  $N_2$  (0–30 s) – humidified  $N_2$  (30–210 s) – dried  $N_2$  (210–360 s).



**Fig. S5:** The time course of normalized  $R$  for CMP and CMP-M (M: Pd, Pt and Au). The dotted line represents normalized RH curve monitored by commercial humidity sensor. In the time course measurements, the gas flow was changed as follows: dried  $N_2$  (0–30 s) – humidified  $N_2$  (30–210 s) – dried  $N_2$  (210–360 s).

## References

- 1 D. Bäuerle, *Laser Processing and Chemistry* (Springer-Verlag Berlin Heidelberg New York 2000)
- 2 <http://www.dupont.com/content/dam/dupont/products-and-services/membranes-and-films/polyimide-films/documents/DEC-Kapton-summary-of-properties.pdf>
- 3 <https://www.entegris.com/resources/assets/6205-7329-0513.pdf>.
- 4 T. Nakajima, T. Tsuchiya and T. Kumagai, *Cryst. Growth Des.*, 2010, **10**, 4861.
- 5 *Materials Safety Data Sheet Solution Center*: <http://www.msds.com/>.