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# Synthesis and Characterization of Fluoro-*co*-Phenyl Silsesquioxane (FCPSQ) for Low Dielectric Constant Materials

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*A new type of low-*k *dielectric material, poly(tridecafluoro1,1,2,2,tetrahydrooctyl-*co*-phenylsilsesquioxane) (PFCPSQ) was synthesized by hydrolysis and condensation reaction of trimethoxysilyl monomers in the presence of a base catalyst in $H_2O$/THF mixture solvent at 25°C. Chemical compositions, molecular weight, and structure of the obtained PFCPSQs were characterized using $^1H$ NMR, $^{29}Si$ NMR, FT-IR, and GPC. Dielectric values were examined by a HP-4190 system and a dielectric constant* k *of 1.92 was obtained.*

**Keywords** Dielectric material; fluorine polymer; silsesquioxane

## Introduction

According to the International Technology Roadmap for Semiconductor (ITRS), by the year 2010 the minimum feature size will be 50 nm, which requires insulation with a dielectric material having a dielectric constant, $k = 2.1$. Presently, several low-$k$ materials are available from various materials suppliers. However, poor processing ability of general dielectric material is still an ongoing problem [1]. An ultra low dielectric material ($k < 2$) will be necessary for future generations of integrated circuits. The effect of a low dielectric constant will be to increase the speed of the signal and improve the density of the packaging, resulting in improved system performance. One of the methods for achieving low dielectric constants is using C–F bond as a functional moiety [2]. In general, fluorine substitution lowered the $k$ value by decreasing the polarizability and increasing the free volume. Insertion of F or $-CF_3$ groups decreases the electronic polarizability due to a strong electron-withdrawing inductive effect. The bulky $-CF_3$ group is able to reduce efficient molecular packing and

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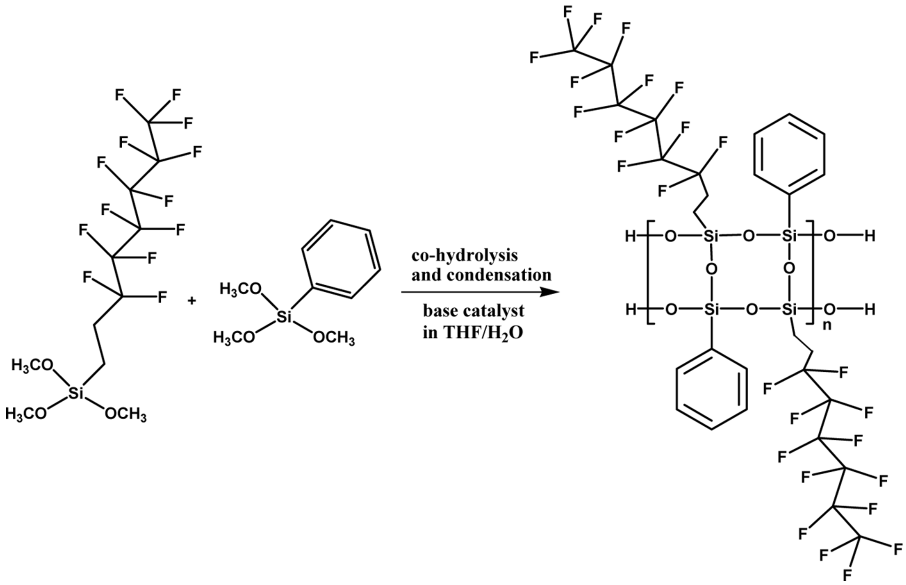

**Scheme 1.** Synthesis of poly(tridecafluoro1,1,2,2-tetrahydrooctyl-*co*-phenylsilsesquioxane) (PFCPSQ).

increase the free volume [3,4]. However, insertion of flexible fluorine groups lead to lower thermal stability and poor processing ability.

Silsesquioxanes, $(RSiO_{1.5})_n$ are an unusual intriguing class of organosilicon compound, which show a unique set of physical, chemical, and molecular size-dependent properties that could not be realized from just ceramic or organic polymer alone [5]. Such properties are prerequisite for electrical components in the semiconductor industry, as it allows easy manufacture of high performance integrated-circuit (IC) devices. To decrease intrinsic dielectric constant more in the matrix, a fluorine introduced silsesquioxane matrix was examined. For this, various poly(tridecafluoro-1,1,2,2-tetrahydrooctyl-*co*-phenyl silsesquioxane) (PFCPSQ) were synthesized by *co*-hydroysis and condensation in the presence of a base catalyst in $H_2O$/THF mixture solvent at 25°C (Scheme 1). The details of the mechanism of monomer hydrolysis followed by condensation will be reported elsewhere [6]. Chemical compositions, molecular weights and structures of the obtained PFCPSQs were characterized using $^1H$ NMR, $^{29}Si$ NMR, FT-IR, and GPC. The dielectric value was examined by HP-4190 system using metal-insulator-metal (MIM) method.

## Experimental

### *Materials*

Tridecafluoro1,1,2,2-tetrahydrooctyl trimethoxysilane and trimethoxy-phenylsilane (Gelest, 98%) were vacuum distilled before use. Tetrahydrofurane (THF) (J.T baker, 99.8%) was distilled from metal sodium with benzophenone before use. Potassium carbonate (sam-jun) was dried overnight along vacuum at 50°C.

### *Synthesis of Poly(tridecafluoro1,1,2,2-tetrahydrooctyl*-co-*phenylsilsesquioxane) (PFCPSQ)*

In a 100 ml round-bottomed flask, deionized water (2.4 g, 0.133 mol) and Potassium-carbonate ($K_2CO_3$) (0.02 g, 0.145 mmol) were charged and stirred for 10 min. Dry THF (4 g, 0.056 mol) was added and stirred for additional 30 min. And then, tridecafluoro1,1,2,2-tetrahydrooctyl trimethoxysilane (TDFTMS) and trimethoxyphenylsilane (TMPS) mixtures (0.04 mol) were added dropwise via syringe under nitrogen and the reaction kept for stirring at room temperature for 72 h. We prepared PFCPSQ samples from different mole-ratios of TDFTMS and TMPS (Table 1). After 72 h the crude was divided into two phases as colorless and white phases. Crude, white, viscous products were obtained by decantation of the colorless mixed solvent.

### *Purification Method of PFCPSQ*

Crude, white, viscous products were dissolved in methylene chloride (M.C) (30 ml) and extracted with deionized water (30 mL) for 2 h. Afterwards, deionized water was removed and M.C solution was dried overnight from $MgSO_4$. The M.C solution was filtered to remove anhydrous $MgSO_4$ and then M.C was evaporated at 40°C. Final white powders were obtained after vacuum drying at 40°C.

### *Dielectric Constant Measurement*

For the dielectric constant measurement, dielectric films were prepared using a spin-coating technique on aluminum (Al) deposited Si-wafer from 1 wt% of THF solution, followed by a drying procedure under vacuum for 5 h at 40°C. Upper Al electrodes with a diameter of 1 mm were deposited on the film surface by a mask-sputtering method to form an Al/dielectric film/Al sandwich structure (MIM structure). The capacitance of the MIM structure was measured by a HP 4192A impedance analyzer from 100 kHz to 1 MHz. Capacitance of the films on aluminum surface was measured at room temperature.

### *Structural Characterization*

The number average molecular weight ($M_n$) and molecular weight distributions ($M_w/M_n$) of the polymers were measured by JASCO PU-2080 plus SEC system

**Table 1.** Mole ratio and properties of the synthetic PFCPSQ series

| Sample | TDFTMS/ TMPS mole ratio | Mn | PDI | 5% weight loss Temp (°C) | [a]Fluorine contents of materials (wt%) | Dielectric constant (1 MHz) |
|---|---|---|---|---|---|---|
| PFCPSQ55 | 5/5 | 3886 | 1.7 | 325 | 45.4 | 1.92 |
| PFCPSQ46 | 4/6 | 1731 | 1.9 | 385 | 40.7 | 2.18 |
| PFCPSQ37 | 3/7 | 2417 | 1.64 | 392 | 34.2 | 2.29 |
| PFCPSQ28 | 2/8 | 1657 | 1.83 | 425 | 20.5 | 2.60 |
| PFCPSQ19 | 1/9 | 1250 | 1.96 | 442 | 14.1 | 2.90 |

[a] calculated by $^1$H-NMR integral calculus.

equipped with RI-2031 plus refractive index detector and a UV-2075 plus UV detector (254 nm detection wavelength) using THF as the mobile phase at 40°C and a flow rate of 1 mL/min. The samples were separated through four Shodex-GPC KF-802, KF-803, KF-804, KF-805. $^1$H NMR and $^{29}$Si NMR spectra were recorded in $CDCl_3$ at 25°C on a Varian Unity INOVA ($^1$H: 300 MHz, $^{29}$Si: 59.6 MHz). FT-IR spectra were measured with a Perkin-Elmer FT-IR system Spectrum-GX using solvent cast films on KBr plates. Thermal gravimetric analysis was performed by TA Instrument TGA 2950 under $N_2$ atmosphere. The X-ray film diffraction was examined at the beam-line 3C2 of Pohang light source (PLS) in the Pohang Accelerator Laboratory (PAL) using Cu-K$\alpha$ radiation.

## Results and Discussion

Figure 1 shows $^1$H-NMR spectra of the various PFCPSQs, respectively. Broad shapes of the proton peaks (a-c) from the phenyl and ethyl groups of the PFCPSQs indicated successful synthesis of various PFCPSQs by the condensation polymerization with the completely hydrolyzed monomer. Furthermore, integrated ratio of phenyl and ethyl groups changed as expected.

$^{29}$Si NMR spectra of PFCPSQs show broad and two large peaks at −68 ppm and −80 ppm, respectively. $T_3$ structure of the phenyl-siloxane bond, Ph-Si(OSi-)$_3$, in Figure 2(a) was assigned to the peak at −80 ppm, while the alkyl-siloxane $T_3$ bond of tridecafluoro1,1,2,2-tetrahydrooctyl moieties, alkyl-Si(OSi-)$_3$, can be assigned to the peak at −68 ppm in Figure 2(b) [7]. It indicated that most of the hydroxyl groups

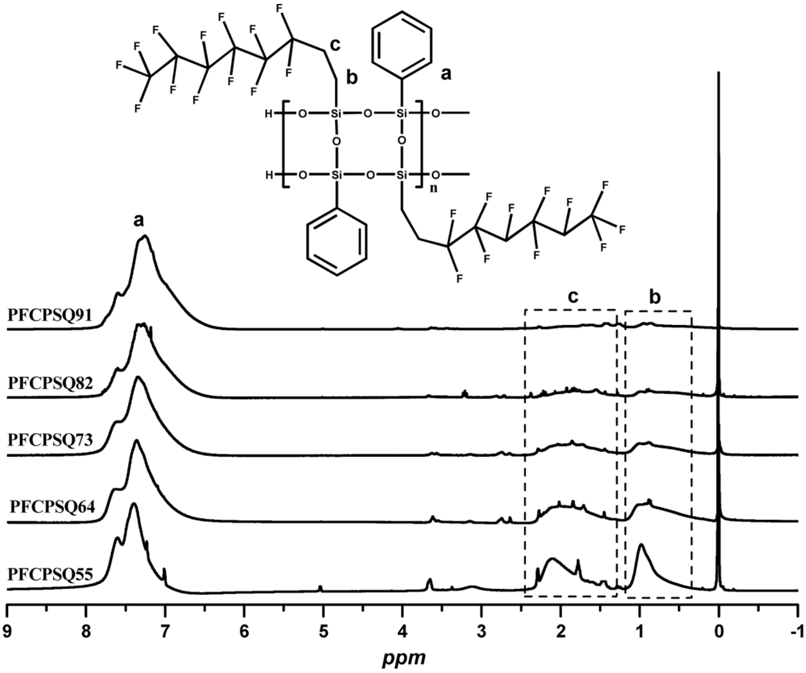

**Figure 1.** $^1$H NMR spectra of poly(tridecafluoro1,1,2,2-tetrahydrooctyl-*co*-phenylsilsesquioxane) in $CDCl_3$.

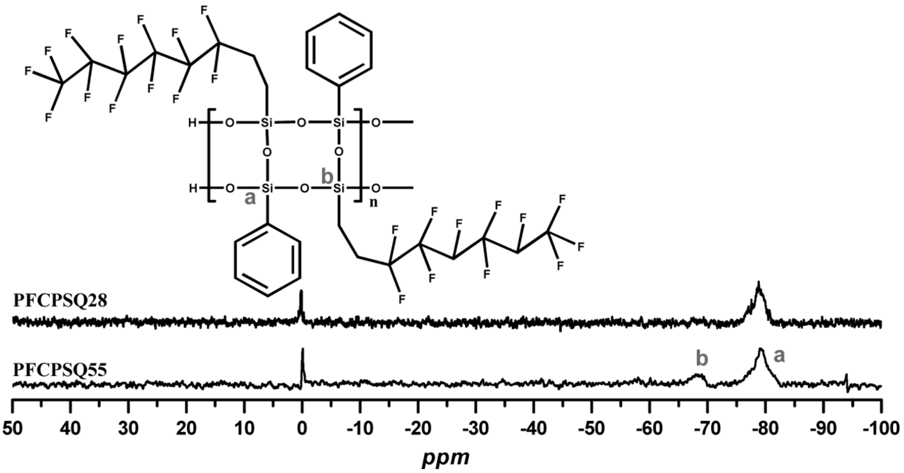

**Figure 2.** $^{29}$Si NMR spectra of poly(tridecafluoro1,1,2,2-tetrahydrooctyl-*co*-phenylsilsesquioxane) in $CDCl_3$.

in the hydrolyzed monomer were consumed for the condensation polymerization to form PFCPSQs of a ladder or cage structure. However, it was observed that as the ratio of TMPS/TDFTMS increases to PFCPSQ82 and PFCPSQ91, the −68 ppm peak assigned to alkyl-siloxane $T_3$ is disappeared.

FT-IR analysis of PFCPSQs also supported the results (Fig. 3). The peak ranging from 1000 to 1200 $cm^{-1}$ originated from the stretching vibration of the −Si−O−Si− bond in the vertical (−Si−O−Si−R) and horizontal (−Si−O−Si−)

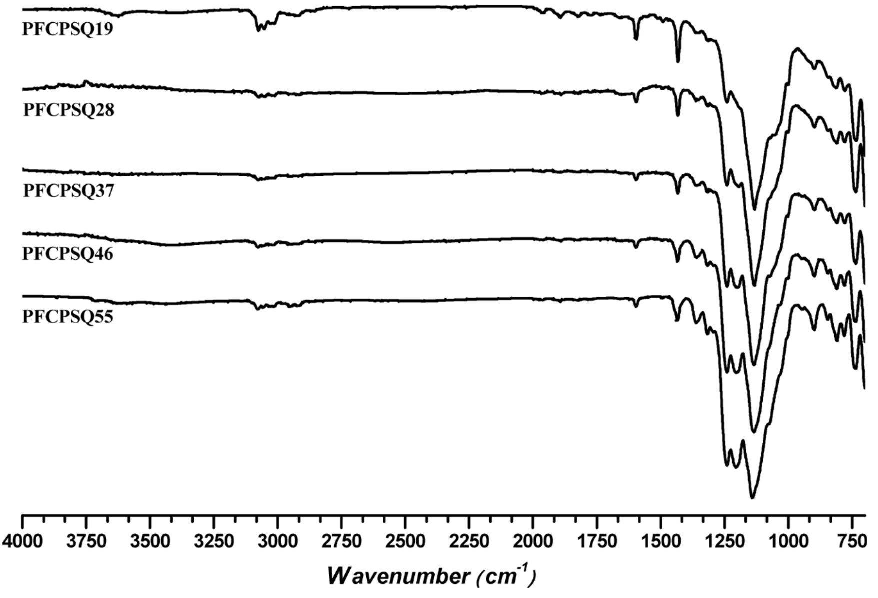

**Figure 3.** FT-IR spectrum of poly(tridecafluoro1,1,2,2-tetrahydrooctyl-*co*-phenylsilsesquioxane)s.

direction of the polysilsesquioxane backbone, indicating that it is one of the structures of the ladder, cage, or random network [8,9]. Here, because the peak portion (intensity) close to $1200\,cm^{-1}$ is larger than that of buried $1000\,cm^{-1}$ peak, the structural regularity of silsesquioxane increased, indicating that there is a greater portion of the ladder-like structure relative to that of the other types of structures. Additionally, C–F stretching vibrations were observed at 1220 and $1250\,cm^{-1}$.

Figure 4 shows the X-ray diffraction (XRD) pattern of the obtained PFCPSQs. According to literature [10], polysilsesquioxane typically show two characteristic diffraction peaks at room temperature. The first sharp peak at 7.3° ($d_1 = 12.1$ Å) comes from the intramolecular periodic chain-to-chain distance (a) in the ladder-structured poly(phenylsilsesquioxane) (LPPSQ). With the second diffusing peak at 18.8° ($d_2 =$ 4.7 Å), a wide range of diffraction angles revealed the average thickness (b) of the ladder-structured polysilsesquioxane. In addition, it was observed that as the TMPS/TDFTMS mole ratio increase, the orderedness of the chain-to-chain distance increased. The most significant difference in crystallinity between PFCPSQ28 and PFCPSQ46 coincided with the largest increase in dielectric constant value.

Figure 5 shows the TGA results for PFCPSQs at a 20°C/min scan rate from 50°C to 800°C under nitrogen. All PFCPSQ copolymers exhibited superior thermal stability. Furthermore, samples exceeding the phenyl molar ratio of PFCPSQ46 exemplified thermal stability up to 400°C. Considering the flexibility and functionality of TDFTMS, this thermal stability is difficult to achieve. However, such outstanding thermal stability was achieved due to the strong silsesquioxnae backbone.

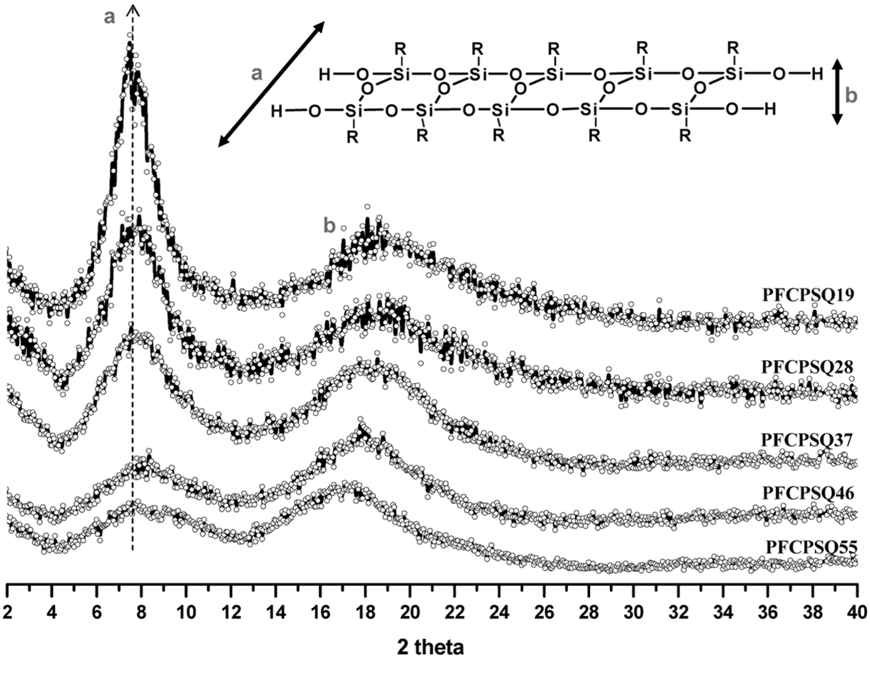

**Figure 4.** XRD pattern of poly(tridecafluoro1,1,2,2-tetrahydrooctyl-*co*-phenylsilsesquioxane)s: periodic chain-to-chain distance (a) and thickness (b).

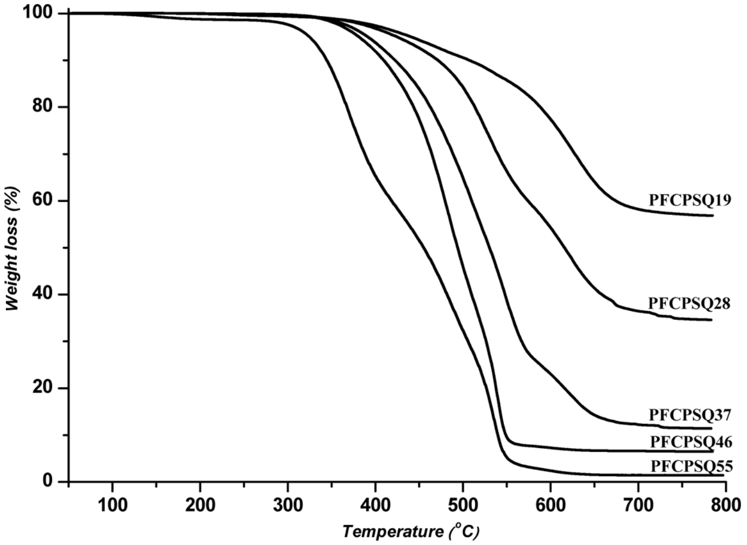

**Figure 5.** TGA thermographs of poly(tridecafluoro1,1,2,2-tetrahydrooctyl-*co*-phenylsilsesquioxane)s.

Figure 6 shows the dielectric constant values of the obtained PFCPSQs. The dielectric constant $k$ of the films was calculated by the formula of a parallel plate capacitor:

$$k = C \times t/k_0 \times A \tag{1}$$

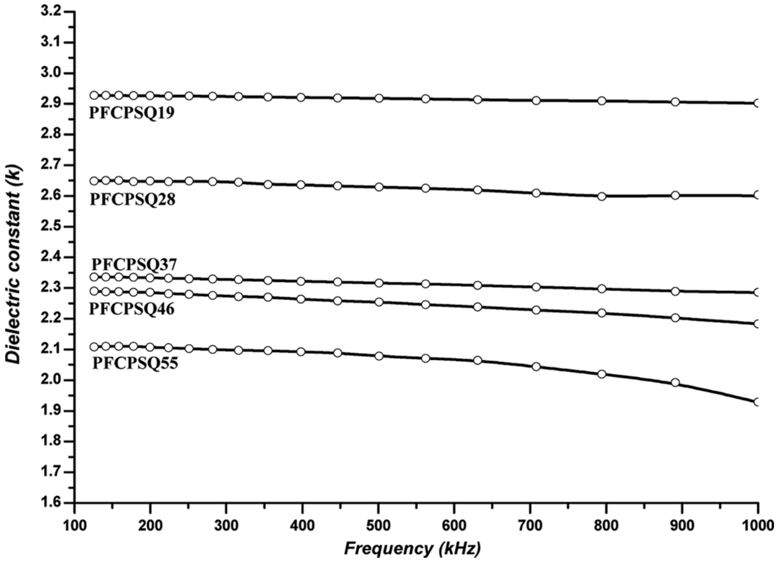

**Figure 6.** Dielectric constant value of poly(tridecafluoro1,1,2,2-tetrahydrooctyl-*co*-phenylsilsesquioxane)s from 100 kHz to 1 MHz.

where $C$ is the capacitance of the MIM element, $t$ is the thickness of the dielectric film, $A$ is the area ($7.58 \times 10^{-7}\,\mathrm{m}^2$) of the Al-electrode, and $k_0$ ($8.854 \times 10^{-12}\,\mathrm{F/m}$) is the permittivity of free space. Averaged data of the dielectric constant for a film was obtained from at least five MIM elements and calculated by (1) [1].

Obtained dielectric constant measurements are shown in Figure 6. Dielectric constant values measured at 1 MHz ranged from 1.92 to 2.9. PFCPSQ55, the copolymer with the greatest fictionalization of fluorine gave a dielectric constant of 1.92, noteworthy of an ultra-low-$k$ material. However, PFCPSQ19, with the largest proportion of phenyl groups gave an elevated dielectric constant of 2.9, which can be attributed to the increasing conjugating effect of the phenyl moiety.

## Conclusion

A fluorine containing silsesquioxane, poly(tridecafluoro1,1,2,2,tetrahydrooctyl-*co*-phenylsilsesquioxane) (PFCPSQ), was successfully synthesized as a low $k$ dielectric material. Five obtained PFCPSQ samples exhibited dielectric constant values ranging from 1.92 to 2.9. Furthermore, obtained PFCPSQ37, PFCPSQ28, and PFCPSQ19 showed outstanding thermal stability exceeding temperatures of 400°C. Therefore, PFCPSQs synthesized by this method are expected to be applicable in a myriad of uses in the semiconductor industry.

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