

# Fabrication of transparent methacrylate zirconium siloxane hybrid materials using sol–gel synthesized oligosiloxane resin

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**Abstract** Methacrylate zirconium siloxane (MZS) resin was synthesized by a sol–gel reaction of 3-(trimethoxysilyl)propyl methacrylate, diphenylsilanediol, and zirconium n-propoxide chelated with methacrylic acid. Also, propylene glycol monomethyl ether acetate was added as a solvent to synthesize a homogeneous and long-term stable resin by controlling the reactivity among the precursors. A High condensation degree of the resin and the formation of Si–O–Zr hetero-metal bonds were verified by  $^{29}\text{Si}$  NMR and FT-IR spectroscopy. The MZS resin was spin-coated and photo-polymerized to fabricate a highly transparent MZS hybrimer coating film. The refractive index and dielectric constant of the film increased according to the zirconium content, up to 1.59 and 3.65, respectively.

**Keywords** Sol–gel hybrid material · Methacrylate zirconium siloxane · Degree of condensation · Optical transparency · High refractive index

## 1 Introduction

Sol–gel derived inorganic–organic hybrid materials (hybrimers) have been extensively researched, as they offer combined benefits of both organic and inorganic characteristics [1–5]. Hybrimers, composed of a siloxane network formed by sol–gel condensation and a polymer network

formed by organic polymerization at a molecular scale, are transparent, and more thermally and mechanically stable than general polymers. Given these characteristics, they have been studied for use as potential optical materials [6–8].

Recently, we reported on siloxane-polymer hybrimers fabricated by curing of organo-oligosiloxane resin synthesized by a sol–gel reaction of organosilanes. The synthesized organo-oligosiloxane resin is mostly condensed and clear with long-term stability due to the absence of hydroxyl radicals. Furthermore, they can be easily processed to produce coatings or bulk samples. Hybrimers fabricated via polymerization of the organo-oligosiloxane resin are good candidates for various optical applications due to their excellent optical properties, such as high transparency, low optical loss, and low birefringence [2, 9–14]. The hybrimer also offers easy tunability of optical and electrical characteristics by controlling the inorganic and organic compositions. Methacrylate hybrimers have been fabricated in previous studies by UV curing of methacrylate phenyl oligosiloxane synthesized by sol–gel condensation of 3-(trimethoxysilyl)propyl methacrylate (MPTS) and diphenylsilanediol (DPSD) [9, 12]. The hybrimer has excellent transparency and a high refractive index (up to 1.56) due to the presence of phenyl groups, allowing versatility in the design of components and materials in micro-optical devices such as optical coatings, micro-lens, waveguides, etc.

These hybrimers, however, have a low dielectric constant due to the existence of symmetrical phenyl groups [13]. Thus, it is necessary to increase the refractive index and dielectric constant while maintaining molecular homogeneity so that they can be effectively utilized in optics and electronics. The simplest method to accomplish this is to add metal (zirconium or titanium) alkoxides

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during fabrication of the hybrimer. However, a precursor solution containing metal alkoxides is not sufficiently stable to fabricate transparent and homogeneous hybrid materials via a sol–gel process due to the active reactivity of the metal alkoxides. Therefore, preparation of a stable and homogeneous precursor solution containing metal for fabrication of hetero-metal siloxane hybrid materials is an important area of research [15–20].

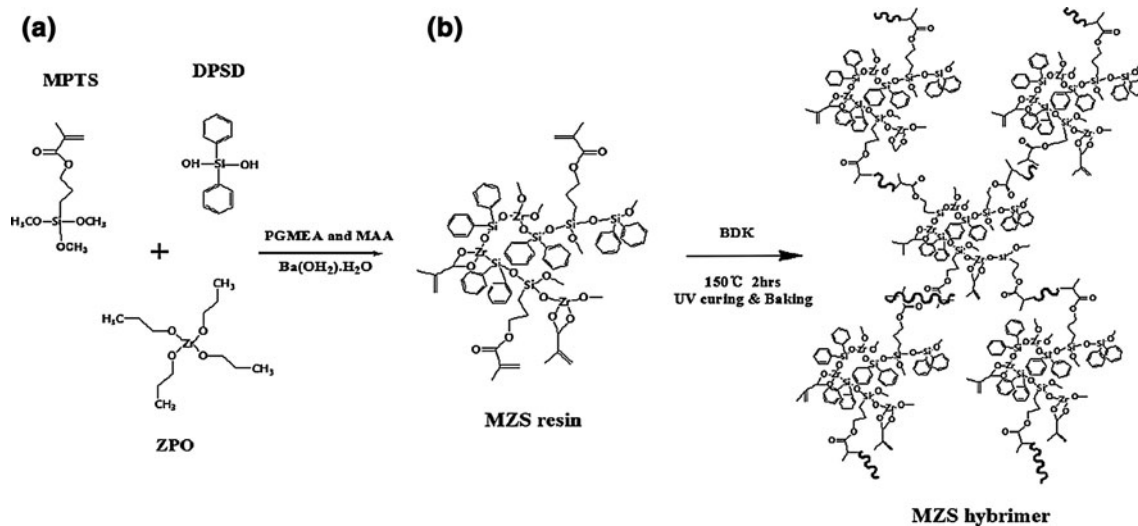
In this study, we synthesized methacrylate-zirconium-oligosiloxane resin by sol–gel reaction of 3-(trimethoxysilyl)propyl methacrylate (MPTS), diphenylsilanediol (DPSD) and zirconium n-propoxide (ZPO) without adding water, as represented in Scheme 1a. Instead of titanium, we incorporated a zirconium precursor, since it does not undergo any catalytic photodegradation of organic groups [20]. Methacrylic acid (MAA) was used as a chelating agent in the presence of a solvent (PGMEA) to increase the degree of condensation and homogeneity. The formation and condensation of Si–O–Zr hetero-metal bonds were thereby promoted during the sol–gel reaction. The synthesized oligosiloxane resin was spin-coated and UV-cured to fabricate a methacrylate zirconium siloxane hybrid (MZS hybrimer) coating film, as described in Scheme 1b. It was found that the refractive index and dielectric

constant of the hybrimer coating film increases according to the Zr content.

## 2 Experimental

### 2.1 Synthesis of methacrylate zirconium siloxane (MZS) resin

Methacrylate zirconium oligosiloxane resin was synthesized by a solvent assisted sol–gel condensation reaction of 3-(trimethoxysilyl)propyl methacrylate (MPTS, Aldrich), diphenylsilanediol (DPSD, Gelest), and zirconium n-propoxide (ZPO, 70% solution in propanol, Aldrich) in molar ratio of 4:6:0, 3:6:1, 2:6:2 and 1:6:3, respectively. The content of the DPSD precursor was fixed at 0.09 mol and ZPO content was increased from 0 to 0.045 mol while the MPTS content was decreased from 0.06 to 0.015 mol, as listed in Table 1. In advance, ZPO was chelated by methacrylic acid (MAA, Aldrich) with a molar ratio of 2:1 to balance the reactivity between MPTS and ZPO. After 1 h stirring, MPTS was added to the chelated ZPO and stirred for a further 20 min at room temperature. Also, DPSD was dissolved in propylene glycol monomethyl



**Scheme 1** a Synthesis of methacrylate zirconium oligosiloxane resin by a solvent assisted sol–gel condensation of MPTS, ZPO and DPSD and b fabrication of methacrylate zirconium siloxane hybrid material (MZS hybrimer)

**Table 1** Compositions of chemicals for synthesis of methacrylate zirconium siloxane resin

MPTS (g)	DPSD (g)	Zirconium n-propoxide (g)	Ba(OH) <sub>2</sub> ·H <sub>2</sub> O (g)	PGMEA (g)
14.9 (0.06 mol)	19.47 (0.09 mol)	0	0.057	58.41
11.18 (0.045 mol)	19.47 (0.09 mol)	7.02 (0.015 mol)	0.057	58.41
7.45 (0.03 mol)	19.47 (0.09 mol)	14.04 (0.03 mol)	0.057	58.41
3.73 (0.015 mol)	19.47 (0.09 mol)	21.06 (0.045 mol)	0.057	58.41

ether acetate (PGMEA, Aldrich) at 80 °C with a 3:1 weight ratio, yielding a clear solution. The DPSD solution was then slowly mixed with the mixture of MPTS and ZPO. The condensation reaction of the mixed solution was performed at 80 °C in the presence of a catalyst, 0.2 mol% of barium hydroxide monohydrate [Ba(OH)<sub>2</sub>·H<sub>2</sub>O, Aldrich], for 10 h. After the reaction, the synthesized resin was filtered through a 0.45 μm Teflon filter to remove the catalysts. Also, by-product of the condensation reaction (methanol) and residual solvent were removed by vacuum heating at 60 °C.

## 2.2 Fabrication of methacrylate zirconium siloxane (MZS) hybrimer film

To fabricate the MZS hybrimer coating film, 2,2-dimethoxy-2-phenyl-acetophenone (BDK, Aldrich) was added to the synthesized resin as a photo-initiator for photopolymerization of the methacrylate groups, as illustrated in Scheme 1b. The content of BDK was 2 wt% of the entire resin. The resin was diluted by PGMEA to reduce its viscosity for easier fabrication of the coating film. The weight ratio of MZS resin to PGMEA was 1:1. The diluted resin was then stirred at room temperature for 8 h and spin-coated at 2,000 rpm for 30 s on various substrates (soda lime glass, ITO glass, and Si wafer). The coated film was photo-cured using an ultraviolet (UV) lamp (500 W Hg Lamp, ~365 nm, Oriel 97453) in a N<sub>2</sub> atmosphere for 3 min. In order to evaporate the residual solvent and non-polymerized organic groups, the film was baked at 150 °C for 2 h. The baking was performed in a vacuum oven to prevent formation of cracks inside the film. After UV-curing and baking, a dense and smooth coating film with high refractive index was successfully fabricated.

## 2.3 Characterization of oligosiloxane resin and hybrimer

The condensation behavior and formation of Si–O–Zr hetero-metal bonds in the oligosiloxane resin were examined through <sup>29</sup>Si Nuclear Magnetic Resonance (NMR) spectroscopy and Fourier Transform-Infrared (FT-IR) spectroscopy (JASCO, FT-IR 460plus). <sup>29</sup>Si NMR spectra of the MZS resin in 30 vol% of chloroform-d were analyzed using a FT 600 MHz (Bruker Biospin DMX600) instrument. Chromium (III) acetylacetonate was added as a relaxation agent with a concentration of 30 mg/L. Also, we performed FT-IR spectra analysis in solution with a resolution of 4 cm<sup>-1</sup> in a wavenumber range of 650–4,000 cm<sup>-1</sup>.

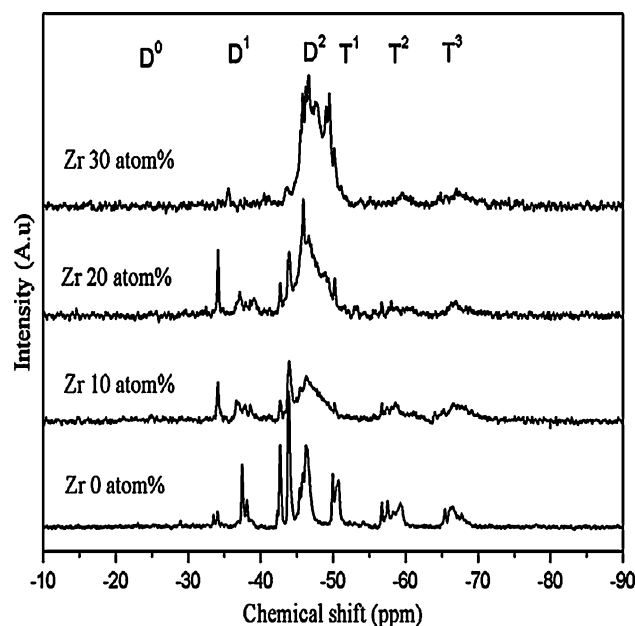
The refractive index of the MZS hybrimer film coated on the Si wafer was obtained by a prism coupler (Pennington, Metricon 2010) at a 633 nm wavelength. The film

was coated on ITO glass to measure its dielectric constant. Circular gold electrodes having a radius of 0.54 nm were deposited by thermal evaporation at a rate of 0.5 Å min<sup>-1</sup>. The dielectric constant was measured with an HP4194A (Agilent Technologies) impedance/gain analyzer and a Keithley 237 source-measure unit (Keithley). The optical transmittance of the film coated on a quartz substrate was obtained in a wavelength range from 300 to 800 nm using an UltraViolet–Visible (UV–Vis) spectrophotometer (Shimadzu, UV3010 PC). Finally, cross-sectional photographs of the coating film were taken by Scanning Electron Microscopy (SEM, Hitachi S-4800) and the surface morphology was also examined using Atomic Force Microscopy (AFM, SEIKO).

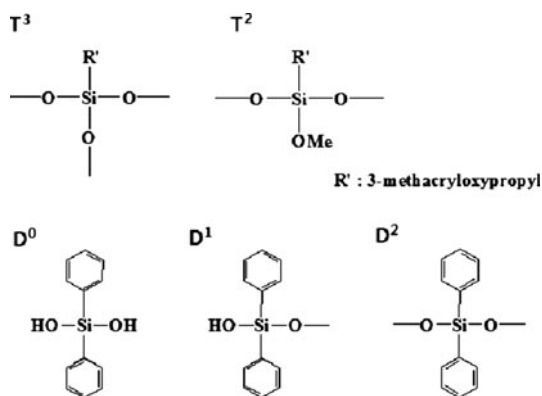
## 3 Results and discussion

### 3.1 Formation of highly condensed methacrylate zirconium oligosiloxane resin

<sup>29</sup>Si NMR spectra of the synthesized oligosiloxanes are shown in Fig. 1 to show the condensation behavior depending on zirconium content. The nomenclatures, T<sup>n</sup> and D<sup>n</sup>, are assigned to Si atoms of MPTS and DPSD in the oligosiloxane structure, as shown in Fig. 2. The superscript, n, denotes the number of siloxane bonds attached to Si atoms. Degree of chemical shifts can be assigned as D<sup>0</sup> (–29 ppm), D<sup>1</sup> (–36 to –38 ppm), D<sup>2</sup> (–42 to –47 ppm),



**Fig. 1** <sup>29</sup>Si NMR spectra of methacrylate zirconium oligosiloxane resins according to the Zr content



**Fig. 2** Nomenclature,  $T_n$  and  $D_n$ , in  $^{29}\text{Si}$  NMR spectra of the oligosiloxane resin

$T^1$  (−49 to −51),  $T^2$  (−57 to −61 ppm) and  $T^3$  (−65 to −69 ppm), respectively.

In the spectra, the band of the major condensed product was detected at  $D^2$ , and this band verifies high degree of condensation of the MZS resins. The intensity of the  $D^2$  bands gradually increases with a reduction of the  $D^1$  and  $T^1$  bands as the Zr content is varied from 10 to 30 atom%. Also, considerable bandwidth broadening of bands, which indicates the incorporation of Zr in the siloxane network, is detected [21, 22]. The bands shift to a lower field due to the formation of Si–O–Zr hetero-metal bonds. As shown in Fig. 1, there is a field shift (−1 to −3 ppm) of  $D^n/T^n$  bands and this effect is maximized in the  $D^2$  bands of the resin with 30 atom% Zr. Therefore, we could conclude that Zr was successfully incorporated in the oligosiloxane structure and there exists mostly condensed  $D^n/T^n$  species inside the MZS resin. The degree of condensation of the resin can be calculated by the following equation [14].

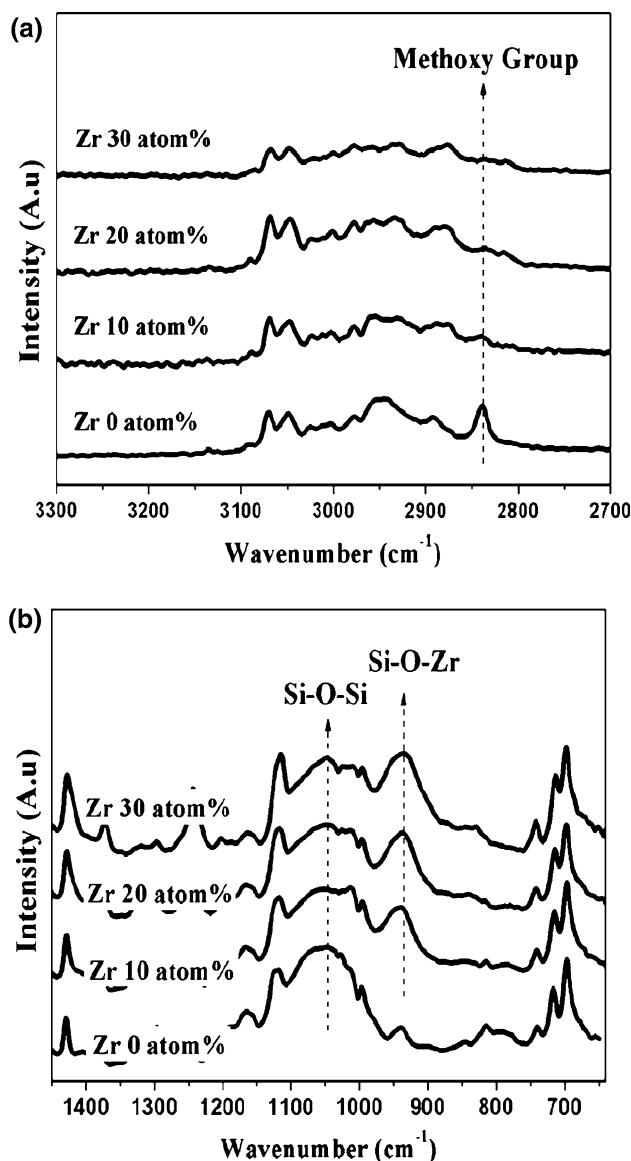
$$\text{DOC} = \frac{D^1 + 2D^2 + T^1 + 2T^2 + 3T^3}{2(D^0 + D^1 + D^2) + 3(T^0 + T^1 + T^2 + T^3)} \times 100$$

Table 2 shows the degree of condensation of MZS resin depending on the resin composition. The degree of condensation increases up to 96.8% with an increase of Zr content up to 30 atom%.

Figure 3 shows FT-IR spectra of MZS resins, presenting further evidence of the formation of Si–O–Zr bonds, where Zr content is varied from 0 to 30 atom%. We could not detect any hydroxyl groups in the spectral regions of 3,600–3,200  $\text{cm}^{-1}$ , assigned to (−OH) vibration of Si–OH. This finding shows that hydroxyl groups are completely removed during the reaction. In the presence of Zr, the intensity of the bands at 2,840  $\text{cm}^{-1}$ , which is assigned to the methoxy (Si–OCH<sub>3</sub>) group, considerably decreases due to complete reaction among the precursors [11]. This

**Table 2** Degree of condensation of methacrylate zirconium oligosiloxane resin and characteristics of MZS hybimer coating film

Zr content (atom %)	DOC (%)	Refractive index (@633 nm)	Dielectric constant (@1 MHz)	Transmittance (@450 nm, %)
0	78.5	1.563	2.98	98.9
10	85.3	1.574	3.39	97.5
20	88.8	1.584	3.50	97.7
30	96.8	1.591	3.65	97.3



**Fig. 3** FT-IR spectra of MZS resins according to the Zr content in a wavenumber range of (a) 2,700–3,300  $\text{cm}^{-1}$  and (b) 650–1,450  $\text{cm}^{-1}$ , where Si–O–Si bonds at 1,065  $\text{cm}^{-1}$  and Si–O–Zr bonds at 940  $\text{cm}^{-1}$

indicates that methoxy groups are changed into Si–O–Zr bonds due to the promoted condensation reaction when Zr is incorporated.

In the spectra, a sharp peak at  $1,110\text{ cm}^{-1}$  and a broad band at around  $1,065\text{ cm}^{-1}$  represent the Si–O–Si asymmetric stretching mode [10]. On the other hand, the bands at  $940\text{ cm}^{-1}$  are assigned to Si–O–Zr hetero-metal bonds [23–25]. As Zr content is increased from 0 atom% to 30 atom%, the relative intensity of Si–O–Zr bands, increases relative to the intensity of Si–O–Si bands. Also, the broad bands at  $1,065\text{ cm}^{-1}$  shift slightly toward bands at  $1,048\text{ cm}^{-1}$  with increasing Zr up to 30 atom%. This is attributed to a field shift of Si–O–Si bands at  $1,065\text{ cm}^{-1}$  towards lower wavenumber resulting from the formation of Si–O–Zr bonds [26]. These band intensity increase and the band position shift is consistent with the hypothesis that the formation of Si–O–Zr hetero-metal bonds is promoted depending on the amount of Zr.

Successful formation of highly condensed MZS resin was achieved by a sol–gel condensation reaction. Si–O–Zr hetero-metal bonds were well formed in the resin by a condensation reaction among the methoxy group of MPTS, the silanol group of DPSD, and the propyl group of ZPO. The ZPO modified by MAA leading to hexacoordinated Zr precursors increase the degree of condensation (Table 2) of zirconium-oligosiloxane resin as compared to pure oligosiloxane resin [21, 22].

In the presence of Zr, it is difficult to match hydrolysis/condensation rates for synthesizing homogeneous and stable MZS resin, because the reactivities of Si and Zr alkoxides are different. Thus, a chelating agent (MAA) was added to produce more Si–O–Zr bonds and to prevent the formation of Zr–O–Zr bonds [20]. However, addition of this agent was not sufficient for controlling the reaction in the presence of large amounts of zirconium alkoxide (>20 atom%). Therefore, we also used a solvent (PGMEA) as a reaction medium to reduce the reaction rate by dilution. Since the reaction rate is function of the concentration of the reactants which depends on the amount of solvent. Through the solvent assisted sol–gel reaction, the synthesized MZS resin shows good long-term stability and a high degree of condensation degree [11], as evidenced by liquid state  $^{29}\text{Si}$  NMR and FT-IR investigations.

In the reaction, the solvent acts as a reaction medium to promote formation of Si–O–Zr bonds which is due to the reaction of Si–OH and ZrOR. Since Zr is more electrophilic than Si, Si–OH reacts more slowly with Si–OR. Also, Zr–O–Zr bonds can be formed due to hydrolysis of Zr–OR by trace of moisture or by ligand exchange with Si–OH. Zr–O–Zr bonds can also result from exchange between Si–O–Zr bonds to give Si–O–Si and Zr–O–Zr, for thermodynamic reasons. Due to the difference in electronegativities between Si and Zr, already formed Si–O–Zr bonds

are more polar compared to Si–O–Si bonds. More polar bonds induce preferred nucleophilic attack of silanol groups in DPSD [18]. Once Si–O–Zr bonds commences, the formation of the hetero-metal bonds is consistently promoted and self-condensation is relatively prohibited [21]. As a result, homogeneously dispersed Si–O–Zr bonds exists in the oligosiloxane structure.

### 3.2 Optical and electrical characteristics of MZS hybri-mer coating films

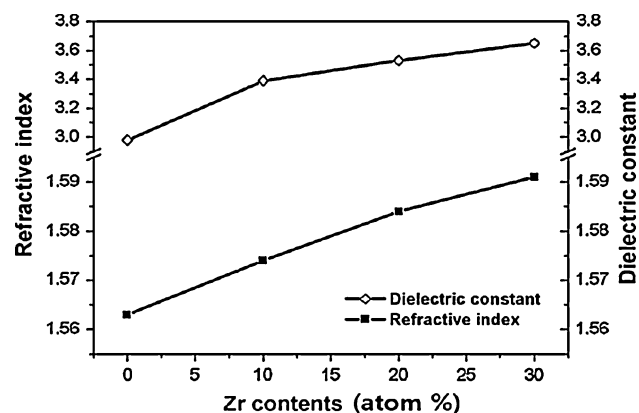
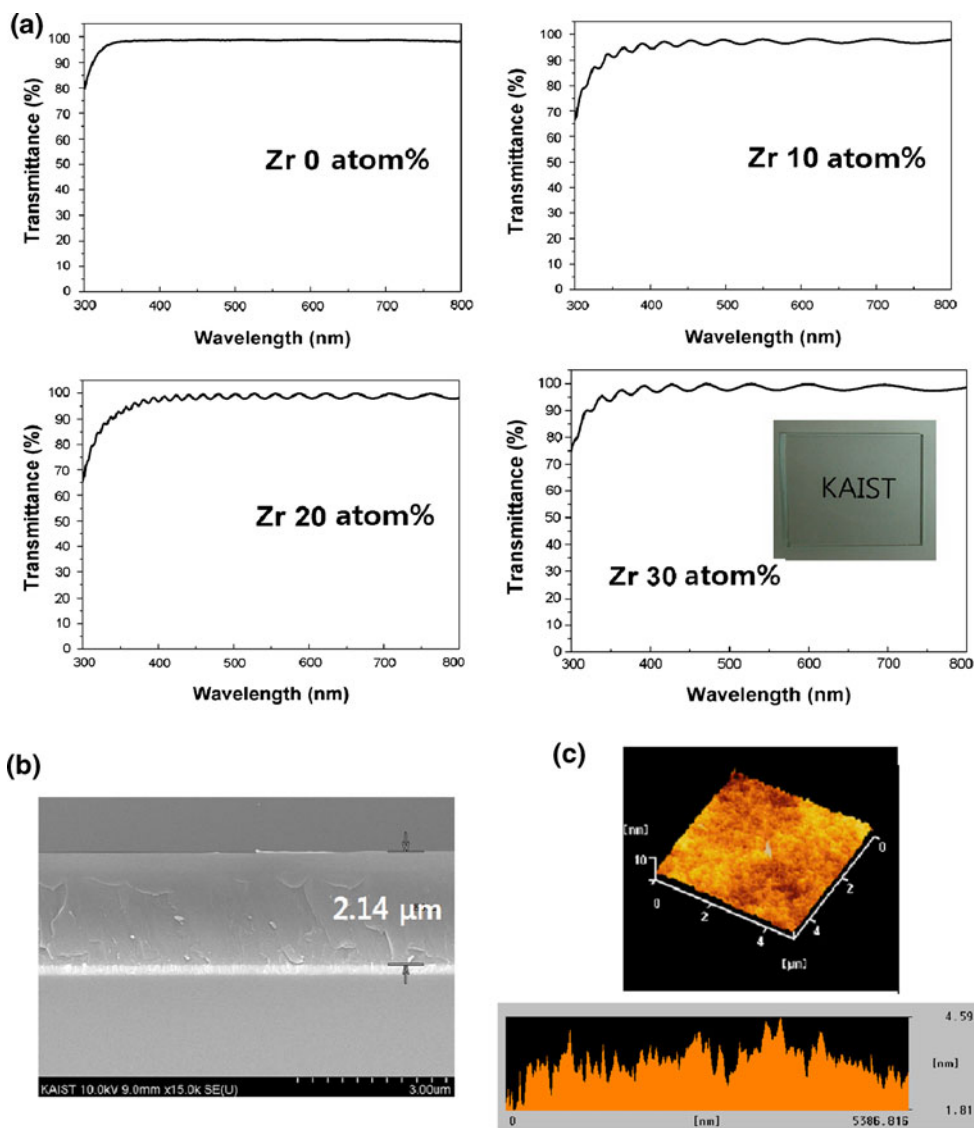
As shown in Scheme. 1b, highly cross-linked MZS hybri-mer is fabricated by photo-polymerization of methacrylate groups between zirconium-oligosiloxanes. The resin is then spin-coated on soda lime glass, Si wafer, and ITO glass to measure optical and electrical characteristics of the coating films. The optical transmittance, refractive index, and dielectric constant of the fabricated films are listed in Table 2 according to the Zr content.

As shown in Fig. 4a, the film is highly transparent for application to various optical devices. It shows excellent transparency over 95% in the visible range regardless of the Zr content. In addition, it is also colorless even when the Zr content is maximized to 30 atom%. In the presence of Zr, high molecular weight zirconium-oligosiloxane exists inside the MZS resin, since ZPO has larger molecular weight than MPTS. These large size molecules prevent photo-polymerization of methacrylate groups due to large steric hindrance [12]. Therefore, the optical transmittance at a wavelength of 450 nm falls slightly due to hindered cross-linking of MZS networks (Table 2).

Also, the MZS hybri-mer coating film shows excellent coating quality, which results in a smooth surface and good adhesion to the substrate, as shown in the cross-sectional SEM image presented in Fig. 4b, c presents an AFM micrograph of the coating film containing 30 atom% Zr. From the image, information on the surface roughness can be obtained. Root-mean-square (rms) surface roughness was measured using AFM line profile data and a value of  $5.56 \times 10^{-1}\text{ nm}$  was obtained in the case of 30 atom% Zr content. This value (rms < 1 nm) verifies surface of MZS hybri-mer film is considerably smooth. Refractive index of the MZS hybri-mer coating film according to the Zr content was also measured at a wavelength of 633 nm, as shown in Fig. 5. A high refractive index is an important factor to develop optically efficient devices. Compared to conventional methacrylate siloxane films fabricated in our laboratory, the refractive index of MZS hybri-mer film considerably increases up to 1.59 in the presence of Zr [14]. As represented in Fig. 5, the refractive index varies from 1.56 to 1.59 with increasing Zr content.

The difference in the refractive index of the films is caused by the microstructure and phase transformations of

**Fig. 4** **a** UV–Vis spectra according to the Zr content and photograph of the MZS resin with 30 atom% of Zr, **b** cross-sectional SEM image and **c** AFM surface image of MZS film with 30 atom% of Zr



**Fig. 5** Refractive index and dielectric constant of MZS hybrimer coating film according to the Zr content

precursor molecules [27]. General fabrication methods require high temperature, which can harm organic groups in hybrid materials. Thus, we focus on the formation of Si–

O–Zr hetero-metal bonds in order to increase the refractive index compared to a pure siloxane network. The refractive index  $n$  can be calculated by the following Lorentz-Lorenz equation [14].

$$\frac{n^2 - 1}{n^2 + 2} = \frac{4\pi}{3} N\alpha$$

where  $n$  is the refractive index,  $N$  is the number of molecules per unit volume, and  $\alpha$  is the mean polarizability. According to the equation, a dense film that has high polarizability shows a high refractive index. In the case of MZS film, there are phenyl groups in DPSD, which shows high electronic polarizability [28, 29]. Furthermore, a sufficient amount of highly polarizable Si–O–Zr bonds are formed when Zr content reaches 30 atom%, as already verified by the FT-IR analysis. Also, photo-polymerization and a thermal curing process can facilitate densification of the film and thereby increase the refractive index [14].

A SEM image of a dense and crack-free MZS hybrimer coating film is shown in Fig. 4b. Although the film contains a large amount of Zr (30 atom%), it is well coated with a smooth surface as shown in the SEM/AFM images.

The thickness of the film was also optimized at 2.14  $\mu\text{m}$  to characterize the dielectric constant (Fig. 4b). The dielectric constant was measured by an impedance/gain analyzer and was found to depend on the Zr content. As shown in Fig. 5, the dielectric constant of the MZS hybrimer film at 1 MHz changes from 2.98 to 3.65 with respect to a change of the content of Zr from 0 to 30 atom%. Tunability of the dielectric constant is useful for many optical applications. We can also incorporate various precursors such as fluorine inside methacrylate oligosiloxane to reduce the dielectric constant. The MZS hybrimer shows a relatively high dielectric constant compared to methacrylate hybrimer ( $\epsilon = 2.98$ ) and fluorinated methacrylate hybrimer ( $\epsilon = 2.54$ ). Note also that the dielectric constant is closely related to the refractive index, as simply shown in the following equation [13].

$$\epsilon = n^2$$

where  $\epsilon$  represents the dielectric constant and  $n$  represents the refractive index. Thus, the dielectric constant is also related to polarizability and density of the film. Similar to the case of the refractive index, more polar Si–O–Zr bonds as compared to Si–O–Si bonds can increase the dielectric constant according to the amount of Zr. As already noted in this paper, densification of the film also increases the refractive index and transparency. A smooth, adhesive, and dense MZS hybrimer coating film was successfully fabricated without cracks, thus yielding superior optical and electrical properties.

#### 4 Conclusion

Highly hetero-condensed methacrylate zirconium siloxane hybrid materials (MZS hybrimers) were successfully synthesized through a solvent assisted sol–gel process. Zr content was increased up to 30 atom% of the entire resin. It was verified that solvent promote balanced condensation reaction among precursors by dilution. In the presence of solvent the reaction rate decreased by diluted concentration of the precursors. Also, Zr alkoxide modified by chelating agent increases the degree of condensation and enhances the formation of hetero-metal Si–O–Zr bonds at a molecular scale. A MZS hybrimer coating film was also fabricated by a photo-polymerization and thermal baking. The film showed excellent transparency and high a refractive index, which are attributed to the high polarizability of Si–O–Zr bonds. The refractive index of the film increased from 1.56 to 1.59 according to the Zr content. Also, the

electrical properties such as dielectric constant were characterized. Therefore, the MZS hybrimer coating films are a suitable candidate for various optical devices and materials such as optical coatings, micro-lens, gratings, and waveguides.

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