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Low-adhesive silicone rubbers for flexible light-emitting devices

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Abstract. In this work, 2-phenylethyl-functionalized (SSR) and 2-methyl-3-methoxy-3--oxopropyl-functionalized silicone rubbers (MSR) were obtained via the platinum(0)-catalyzed hydrosilylation reaction between styrene/methyl methacrylate and polymethylhydrosiloxane. SSR exhibits both sufficient elongation at break ($\varepsilon = 45 \pm 5\%$), tensile strength ($\sigma = 1.5 \pm 0.4$ MPa) and Young's modulus, ($E = 3.4 \pm 0.7$ MPa), which is higher than for Sylgard 184 ($E = 1.1 \pm 0.3$ MPa). SSR and MSR are optically transparent and exhibit a low adhesion to a Si substrate. However, MSR possesses lower tensile strength ($\sigma = 0.6 \pm 0.1$MPa, $E = 0.6 \pm 0.1$ MPa) comparing to SSR. Thus, SSR was applied as a supporting polymer matrix for encapsulation of inorganic NWs arrays for flexible optoelectronics.

Keywords: catalytic hydrosylilation, polysiloxanes, nanowires, light-emitting diodes

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Низко-адгезионные силиконовые резины для гибких светоизлучающих устройств

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Аннотация. В работе представлены 2-фенилэтил- (SSR) и 2-метил-3-метокси-3--оксопропил-функционализированные силиконовые резины (MSR). SSR и MSR были получены с помощью реакции каталитического гидросилилирования между стиролом или метилметакрилатом и полиметилгидросилоксаном в присутствии комплекса платины(0). SSR демонстрирует требуемые относительное удлинение при разрыве ($\varepsilon = 45 \pm 5\%$), предел прочности при растяжении ($\sigma = 1.5 \pm 0.4$ МПа) и модуль Юнга ($E = 3.4 \pm 0.7$ МПа), значения которого превышают значения для Sylgard 184 (E = 1.1 ± 0.3 МПа). SSR и MSR являются оптически прозрачными в видимой спектральной области, а также обладают уменьшенной адгезией к ростовой кремниевой подложке. Однако MSR имеет более низкую механическую прочности (σ = 0.6 ± 0.1 МПа, E = 0.6 ± 0.1 МПа) по сравнению с SSR. Таким образом, SSR был использован в качестве поддерживающей полимерной матрицы для гибких светоизучающих устройств на основе полупроводниковых нитевидных нанокристаллов.

Ключевые слова: каталитическое гидросилилирование, полисилоксаны, светодиоды

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Introduction

Commercial silicone rubbers on the base of polydimethylsiloxanes (PDMSs) such as Dow Corning Sylgard 184 usually are employed as supporting flexible transparent membrane for flexible nanowires (NWs)-based light-emitting devises [1–3] due to the transparency and relatively good elastic properties [4]. However, the commercial PDMS product Sylgard 184 demonstrates a high adhesion to a silicon substrate hampering the membrane release. These factors determine the high demand for development of new durable transparent polymer materials for manufacturing technology of thin membrane/NWs–based devices.

Modification of polysiloxanes by their reaction with various vinyl monomers leads to the increased mechanical strength and reduced adhesion to Si [5].

Materials and Methods

Materials: polymethylhydrosiloxane (PMHS) (number average molecular weight M_n = 1700–3200 g·mol^{-1}, viscosity 12–45 cSt, Sigma-Aldrich, St. Louis, USA), α,ω-di(dimethylvinylsiloxy)polydimethylsiloxane (v-PDMS) (weight-average molecular weight M_w = 25000 g·mol^{-1}, viscosity 850–1150 cSt at 25 °C, Sigma Aldrich, St. Louis, USA), Karstedt's catalyst (platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex) solution 0.1 M in xylene (ABCR GmbH, Karlsruhe, Germany), styrene and methyl methacrylate (ReagentPlus®, contains 4-tert-butylcatechol as stabilizer, ≥ 99%), SYLGARD™ 184 Silicone Elastomer Kit (Dow Corning, Midland, Michigan, USA), and dimethyl sulfoxide (DMSO, ≥ 99%, Vekton, Saint Petersburg, Russia) were purchased from commercial suppliers and their purity was checked by ^{1}H and ^{13}C NMR spectroscopy before usage. Anhydrous toluene (Vekton, Saint Petersburg, Russia) was distilled over sodium-benzophenone ketyl prior to use.

Methods:

Details about molecular beam epitaxy (MBE) of GaP NWs, $CsPbBr_3$ perovskite layer fabrication and SWCNT film synthesis are precisely described in the following reference [6].

Spectroscopy equipment and studies

The NMR spectra were recorded on Bruker AVANCE III 400 spectrometers in $CDCl_3$ at 25 °C at 400 MHz for ^{1}H, 100 MHz for ^{13}C, 80 MHz for ^{29}Si NMR spectra, respectively.

Swelling measurements

The empty pycnometer was preliminarily rinsed with distilled water, dried, and its weight was measured. The pycnometer was filled up to the mark with distilled water and its mass with water was determined. The mass of silicone rubber (m) was estimated as follows: pieces of silicone rubber were placed in a pycnometer with water, and excess water was removed using filter paper, and the mass of the pycnometer was determined together with water and a sample. The density of polymer sample (ρ) was determined by the following equation:

$$\rho = \frac{m}{m_1 + m - m_3} \cdot \rho_0, \tag{1}$$

where $\rho_0 = 0.997$ g·cm^{-3} is density of distilled water at room temperature (20, RT).

Samples (rectangles 10 mm long and 3 mm width) were weighed to estimate the initial dry weight (m_{unex}). Toluene (approximately 270 mL) was added to a round bottom flask that was attached to a Soxhlet extractor and reflux condenser. The sample was loaded into a Soxhlet extractor. The solvent was boiled under reflux in a heating mantle for 2 h. After stopping boiling, the sample was removed and immediately weighed (m_s). Sample swelling percentage was calculated using the following equation:

$$s(\%) = \frac{m_s}{m_{unex}} \cdot 100, \tag{2}$$

Then the sample was dried overnight at RT, then dried for 12 h at 120 °C and reweighed (m_{ex}). Soluble fraction (w_{sol}) and polymer fraction (υ) in the swollen sample were calculated as follows:

$$w_{sol}(\%) = \frac{m_{unex} - m_{ex}}{m_{unex}} \cdot 100, \tag{3}$$

$$\nu = \left[1 + \frac{m_s - m_{ex}}{m_{ex}} \cdot \frac{\rho_p}{\rho_s} \right]^{-1}, \tag{4}$$

where ρ_s and ρ_p – densities of the solvent (toluene, 0.87 g·cm^{-3}) and polymers, respectively.

Tensile properties studies and instruments

Tension tests were conducted on a Shimadzu EZ-L-5kN universal testing machine at a constant cross-head speed of 40 mm/min. At least five measurements were made on each polymer sample according to the ISO 37 type 3 standard.

Thin film processing

Thin membranes of SSR25/GaP NWs and MSR25/GaP NWs were obtained with G-coating.

Adhesion study

Adhesion properties were studied with atomic force microscopy (AFM) approach/retract curves analysis. AFM approach/retraction curves were measured and analyzed on Bruker AFM with standard Si cantilevers (TipsNano HA_CNC B, Cantilever length 184 ± 2 μm, Cantilever width 34 ± 3 μm).

Results and Discussion

The transparent SSR were obtained by a two-step procedure of the platinum(0)-catalyzed hydrosilylation reaction between styrene and polymethylhydrosiloxane giving poly(methylhydrosiloxane-*co*-methyl(2-phenylethyl)siloxane) (S-PMHS). The molar ratios of Si-H (PMHS) and styrene vinyl groups (1:1) were selected to achieve the content of phenylethyl substituents 50%. In order to obtain transparent phenylethyl-functionalized silicone rubber (SSR) S-PMHS was cross-linked with *v*-PDMS. The content of phenylethyl groups in the formed SSR is 25 mol.% (SSR25). Synthesis procedure along with structure and cross-links determination are presented in [6].

The transparent functionalized silicone rubber with the content of 2-methyl-3-methoxy-3-oxopropyl groups equal 25 mol.% (MSR25) was obtained analogously via described above method. The swelling data indicates a correlation between values of a swelling percentage (s), a soluble fraction content (w_{sol}), and a fraction of the polymer in the swollen sample (υ) (Table 1). SSR25 exhibits a lower s and w_{sol}, but higher υ in comparison with MSR25. Therefore, SSR25 is characterized by a larger amount of the cross-links (because of higher content of the starting Si-H groups in S-PMHS in the polymer network). Sylgard 184 and SSR25 demonstrated comparable swelling values.

The tensile properties of the studied rubbers are shown in Table 1. SSR25 exhibits a lower elongation at break (ε), but higher tensile strength (σ) in comparison with MSR25, which is in good agreement with the swelling data for the samples. SSR25 has comparable to Sylgard 184

Table 1

Swelling and tensile properties of silicone rubbers

Silicone rubber	Swelling properties				Tensile properties		
	ρ, $g\cdot cm^{-3}$	s, %	w_{sol}, %	υ	ε, %	σ, MPa	E, MPa
SSR25	1.21 ±0.32	166 ±2	3.0 ±0.7	0.50 ±0.01	45 ±5	1.5 ±0.4	3.4 ±0.7
MSR25	1.05 ±0.01	281 ±13	10 ±0.6	0.30 ±0.01	90 ±19	0.6 ±0.1	0.6 ±0.1
Sylgard 184	1.00 ±0.01	190 ±21	4.1 ±0.4	0.48 ±0.01	92 ±8	2.4 ±0.6	1.1 ±0.3

tensile strength σ and higher Young's modulus (E). Thus, SSR25 can be more preferable as polymer matrix material than MSR25.

The adhesion to the silicon substrate was determined by analyzing the AFM approach/retraction curves. The adhesion force of cantilever to polymer layers can be estimated as the product of the distance between A and B points on corresponding retract curves and the constant spring value of the used AFM tip (Fig. 1.). SSR25 exhibits the lowest adhesion among the studied silicone rubbers with corresponding value of 0.55 of Sylgard 184 adhesion value. MSR25 possesses a slightly higher adhesion (0.66 of Sylgard 184 adhesion value), but still more advantageous than commercial Sylgard 184.

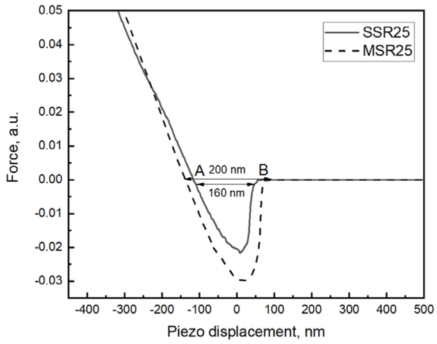

Fig. 1. AFM approach/retract curves of SSR25 and MSR25

UV-Vis spectra of functionalized silicone rubbers indicate no absorption in visible spectral range (see inserts in Fig. 2). According to scanning electron microscopy (SEM) study MSR25 and SSR25 have uniform morphology (Fig. 2) and no spherical structure formation.

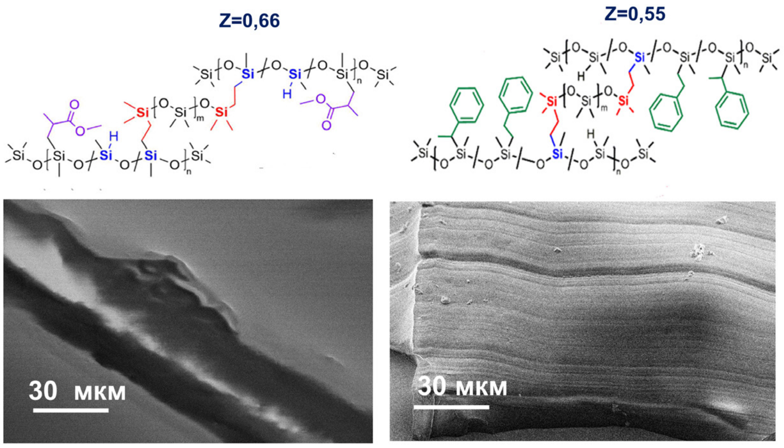

Fig. 2. SEM image of MSR25(left) and SSR25(right) films and their UV-Vis spectra

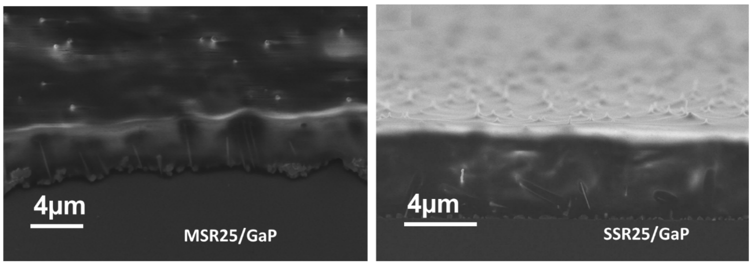

Fig. 3. SEM image of MSR25 and SSR25 films with encapsulated NWs array SSR25 has advantages in tensile properties and was chosen as supporting polymer matrix for GaP/$CsPbBr_3$ based flexible green LED

Thus, transparency and film uniformity along with the reduced adhesion allows to use these polymers for NWs encapsulation. MSR25 and SSR25 both display sufficient encapsulation properties of NWs array (Fig. 3). GaP NWs arrays were encapsulated into MSR25 and SSR25 with G-coating method [5].

Due to the advantages in tensile properties, SSR25/GaP was chosen over MSR25/GaP and employed as flexible transparent contacts for green air-stable perovskite-based LED [6].

Conclusion

Transparent functionalized silicone rubbers SSR25 and MSR25 were obtained via the platinum(0)-catalyzed hydrosilylation reaction between styrene/methyl methacrylate and polymethylhydrosiloxane and cross-linked with v-PDMS. SSR25 and MSR25 show lower adhesion to Si substrate in comparison with Sylgard 184 value ($Z = 1$) – 0.55 and 0.66, respectively. SSR25 exhibits both sufficient elongation at break ($\varepsilon = 45 \pm 5\%$) and tensile strength ($\sigma = 1.5 \pm 0.4$ MPa, $E = 3.4 \pm 0.7$ MPa), which is the main advantage over MSR25.The combination of these useful properties determines the applicability of SSR25 as a supporting polymer matrix for encapsulation arrays of inorganic NWs for flexible optoelectronics.

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REFERENCES

1. **Kochetkov F. M., Neplokh V., Mastalieva V. A., Mukhangali S., Vorob'ev A. A., Uvarov A. V., Komissarenko F. E., Mitin D. M., Kapoor A., Eymery J., Amador-Mendez N., Durand C., Krasnikov D., Nasibulin A. G., Tchernycheva M., Mukhin I. S.,** Stretchable Transparent Light-Emitting Diodes Based on InGaN/GaN Quantum Well Microwires and Carbon Nanotube Films, Nanomaterials. 11 (2021) 1503.

2. **Neplokh V., Fedorov V., Mozharov A., Kochetkov F., Shugurov K., Moiseev E., Amador-Mendez N., Statsenko T., Morozova S., Krasnikov D., Nasibulin A. G., Islamova R., Cirlin G., Tchernycheva M., Mukhin I.,** Red GaPAs/GaP Nanowire-Based Flexible Light-Emitting Diodes, Nanomaterials. 11 (2021) 2549.

3. **Dai X., Messanvi A., Zhang H., Durand C., Eymery J., Bougerol C., Julien F. H., Tchernycheva M.,** Flexible Light-Emitting Diodes Based on Vertical Nitride Nanowires, Nano Lett. 15 (2015) 6958–6964.

4. **Ren Z., Yan S.,** Polysiloxanes for optoelectronic applications, Progress in Materials Science. 83 (2016) 383–416.

5. **Neplokh V., Kochetkov F. M., Deriabin K. V., Fedorov V. V., Bolshakov A. D., Eliseev I. E., Mikhailovskii V. Y., Ilatovskii D. A., Krasnikov D. V., Tchernycheva M., Cirlin G. E., Nasibulin A. G., Mukhin I. S., Islamova R. M.,** Modified silicone rubber for fabrication and contacting of flexible suspended membranes of n-/p-GaP nanowires with a single-walled carbon nanotube transparent contact, J. Mater. Chem. C. 8 (2020) 3764–3772.

6. **Miroshnichenko A. S., Deriabin K. V., Baeva M., Kochetkov F. M., Neplokh V., Fedorov V. V., Mozharov A. M., Koval O. Yu., Krasnikov D. V., Sharov V. A., Filatov N. A., Gets D. S., Nasibulin A. G., Makarov S. V., Mukhin I. S., Kukushkin V. Yu., Islamova R. M.,** Flexible Perovskite $CsPbBr_3$ Light Emitting Devices Integrated with GaP Nanowire Arrays in Highly Transparent and Durable Functionalized Silicones, J. Phys. Chem. Lett. (2021) 9672–9676.

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