# Plasmonic-Organic-Hybrid (POH) Modulators - a Powerful Platform for Next-Generation Integrated Circuits

Claudia Hoessbacher<sup>1</sup>, Patrick Habegger<sup>1</sup>, Marcel Destraz<sup>1</sup>, Scott R. Hammond<sup>2</sup>, Lewis E. Johnson<sup>2</sup>, Norbert Meier<sup>1</sup>, Eva De Leo<sup>1</sup>, Benedikt Baeuerle<sup>1</sup>, Wolfgang Heni<sup>1</sup>

<sup>1</sup>Polariton Technologies Ltd., c/o ETH Zurich, Saeumerstrasse 4, 8803 Rueschlikon, Switzerland <sup>2</sup>Nonlinear Materials Corporation, 2212 Queen Anne Ave North, 98109 Seattle WA, USA Corresponding author: claudia@polariton.ch

**Abstract:** We present reliability studies of plasmonic-organic-hybrid modulators for high-speed optical communications. By exclusion of oxygen and water, demanding thermal environments and high optical power levels can be tolerated. © 2021 The Author(s)

## 1. Introduction

Electro-optic modulators are key components for applications such as high-speed optical communications and sensing [1]. They are traditionally implemented with crystalline electro-optic (EO) materials that lack inversion symmetry such as lithium niobate and rely on the Pockels effect (linear electro-optic effect). The Pockels effect changes the refractive index of the EO material upon an applied electric field, which in turn alters the phase of an optical signal. Recently, hybrid solutions that are combining Pockels-type EO materials with integrated waveguides have gained interest by the research community and industry [2]. Examples comprise the combination of nanophotonic waveguides with organic materials (silicon-organic hybrid, SOH and plasmonic organic hybrid, POH), lithium-niobate thin films (LiNbO3) and barium titanate layers (BaTiO3). Organic electro-optic (OEO) materials have several key differences compared to inorganic crystals. Their most significant advantages are the very high nonlinearities and the enormous intrinsic bandwidths [3]. The strength of response of a Pockels material is characterized by its EO coefficient, with  $r_{33}$  being the metric when the direction of the applied electric field and the refractive index change coincide. The larger this parameter, the smaller the required voltage for a given index change. Typical  $r_{33}$  values for lithium niobate are 34 pm/V [4]. In contrast, polymer devices have shown  $r_{33}$  values over 200 pm/V [5, 6]. Another advantage of OEO materials is their ease of processing, as their solubility means they can be readily coated or printed onto various substrates in large scale. Still, organic materials are new to the communications industry which is reluctant to accept them fearing lifetime issues. While organic optoelectronic materials are used in light-emitting diodes (OLEDs) and digital displays, reliability during processing, storage, and operation needs to be proven for communications applications. This requires precise reliability testing to establish thermal and optical power limits. Previous studies suggested that greater than 10 years stability can be achieved with OEO materials under the exclusion of oxygen even at high optical powers [7]. While those studies are promising, they were conducted on bulk material only and not in nanophotonic waveguides during operation. In another study [8], in-device aging effects were investigated while operating a modulator. Stability at 85 °C for 25 years was concluded, but the efficiency of the material used was rather low. Recently, operation up to 110 °C and storage for 100 h at 90°C was demonstrated using a silicon-polymer hybrid modulator [9]. Further, long-time stability of a polymer/sol-gel modulator was shown without degradation for a duration of 2 years, when storing the device at room temperature and in air [10]. However, data for in-device operation remains to be demonstrated.

In this paper, we present recent results of the OEO material HLD at temperatures up to 120 °C and in-device reliability studies in POH modulators. If water and oxygen are excluded, OEO materials can tolerate demanding thermal environments and high optical power levels.

## 2. Plasmonic-organic hybrid (POH) modulators

Plasmonic-organic hybrid (POH) electro-optic modulators combine plasmonic metal-insulator-metal (MIM) slot waveguides with OEO materials. A plasmonic phase modulator (PPM) [11], consists of two metallic electrodes separated by a narrow slot in which the OEO material is integrated, see Fig 1. This configuration is particularly suited for EO modulators, as the metals forming the plasmonic waveguide can directly serve as electrical contacts. When a voltage is applied across the contacts, the refractive index of the EO material in the slot changes due to the Pockels effect, inducing a phase change of the transmitted light. A PPM can be integrated into a Mach-Zehnder interferometer to translate the phase into an amplitude modulation.

The stability and reliability of OEO devices depends in large part on the stability of the material  $r_{33}$ , which can be broken down into two distinct components; the first relating to the chemical stability of the OEO material, and the second relating to the orientational stability of the acentric alignment of the dipolar chromophores that comprise the OEO material. The  $r_{33}$  of an OEO material can be described by:



Fig. 1 Plasmonic phase modulator (PPM) in the plasmonic-organic hybrid (POH) configuration. Two metallic electrodes are separated by a narrow slot filled with an OEO material. When an electric field is applied across the slot, the plasmonic mode travelling along the metal-insulator-metal waveguide experiences a phase shift due to the Pockels effect. Encapsulation protects the OEO material against environmental influences.

 $r_{33} = \beta_{zzz} \rho_N < \cos^3 \theta > G$ , where  $\beta_{zzz}$  is the molecular hyperpolarizability describing the nonlinear activity of the individual chromophores,  $\rho_N$  is the number density of the chromophores,  $\langle \cos^3 \theta \rangle$  describes the degree of acentric alignment of the chromophores, and G describes local field factors [12]. Any chemical degradation of the chromophores will reduce the effective  $\rho_N$  of active material. When first prepared, a film of OEO material is initially isotropic, and hence the  $\langle \cos^3 \theta \rangle$  and  $r_{33}$  are zero. In order to align the chromophores, the OEO material is electrically poled: heated to its glass transition temperature ( $T_{\rm g}$ ) under application of a large electric field (~ 100 V/µm), at which point the strongly dipolar chromophores can re-orient in response to the external field to yield a non-zero  $\langle \cos^3\theta \rangle$ , and hence  $r_{33}$ . The material is then cooled below  $T_g$  to lock the order in place before the field is removed. Without the poling field, however, any subsequent local molecular motion will be driven towards centrosymmetric alignment by strong chromophore dipole-dipole interactions, and will lead to a loss of  $\langle \cos^3 \theta \rangle$  and  $r_{13}$ . Thus, the OEO material must be protected from temperatures approaching the  $T_0$  after poling. One promising avenue to address this issue is the use of lattice-hardening crosslinking reactions to substantially increase the  $T_g$  during or after poling [13]. The POH design also enables the possibility of local encapsulation of the OEO material through selective area deposition of appropriate encapsulation layers to prevent chemical degradation. This approach may prove to be cheaper than conventional hermetic packaging.

#### 2. Long-term operation

In order to achieve acceptance in the telecommunications community, packaged OEO devices must ultimately be qualified according to Telecordia GR-468 CORE testing standards. Towards this end, bulk parallel plate capacitor devices (glass/ITO/TiO2/OEO/Au) containing a ~1 µm-thick film of the commercial OEO material HLD were prepared [13]. HLD undergoes a Diels-Alder crosslinking reaction at elevated temperatures, which enables the  $T_g$  to be raised as high as  $\sim 160$  °C. The  $r_{33}$  of such parallel plate devices was characterized initially via Simple Reflection, [14] and at regular intervals during storage. Initially, nine such devices were stored at 85 °C in either a N2 atmosphere (Fig. 2(a)) or ambient atmosphere (not shown) for 2000 hrs. The devices stored in N<sub>2</sub> showed no loss of r<sub>33</sub> over 2000 hrs, indicating both perfect chemical and orientational stability of the chromophores at this temperature. In contrast, the devices stored in ambient atmosphere showed  $\sim$ 33% decrease in  $r_{33}$ , which can be conclusively assigned to chemical degradation of chromophores, indicating a need for protection from water and/or oxygen. Subsequently, new devices (≥5 per temperature) were prepared and stored at 105 °C and 120 °C under N2 atmospheres. While these experiments are still underway, the devices are currently showing >90% (105 °C) and >85% (120 °C)  $r_{33}$  retained after ~ 840 hrs (Fig. 2(a)). It is currently not possible to conclusively attribute the loss in performance to either chemical degradation or loss of orientation, but it should be noted that devices are exposed to ambient atmosphere during the regular testing intervals. Regardless, these results show excellent stability of the OEO material  $r_{33}$  under inert conditions even at very high temperatures.

Long-term operation of a POH Mach-Zehnder modulator was evaluated by operating the sample in a controlled environment (nitrogen atmosphere at room temperature), see Fig. 2(b). No further protection and no crosslinking was applied. The device was operated at 1550 nm and 0 dBm optical input power by applying a sinusoidal RF signal of 0 dBm.  $V_{\pi}$  was determined by applying  $\pm 2$  V and measuring the shift of the optical power spectrum. After that, we normalize to the first data point. The variation of  $V_{\pi}$  stayed within  $\pm 20\%$  over 5000 hrs. In Fig. 2(c), we show first results of operation in ambient atmosphere by plotting the degradation slope of the normalized  $V_{\pi}$  over the optical input power at room temperature. We compare two different devices: without encapsulation and crosslinking (blue) and with both encapsulation and crosslinking (red). The degradation slope was determined by a linear fit to the normalized  $V_{\pi}$ -over-time curve. The measurement duration was adapted to the strength of the degradation; for the lower power levels the devices were operated over several days; for the highest power level the slope could be determined after six hours already. Note that for the encapsulated device, a phase modulator was used instead of a Mach-Zehnder modulator and  $V_{\pi}$  was determined via the peak-to-sideband ratio while applying an RF signal. The slot of the waveguide was ~25 nm wider than for the non-encapsulated device. These first results indicate that with the exclusion of oxygen and water high optical power levels can be applied.



Fig. 2(a) Thermal stability of commercial OEO material HLD under N<sub>2</sub>, with 0% loss in r<sub>33</sub> after 2000 h at 85 °C, ~10% loss in r<sub>33</sub> after 840 hrs at 105 °C, and ~15% loss in r<sub>33</sub> after 840 hrs at 120 °C. (b) In-device long-term stability at room temperature and under N<sub>2</sub> without crosslinking. (c) Operation in air for POH modulators. High optical input power levels can be achieved with encapsulation and crosslinking.

#### 5. Conclusion

We demonstrated long-term stability of the OEO material HLD at 85 °C in N2 atmosphere. We have shown stable operation of POH modulators over 5000 h in N2 environment and first optical input-power tests of plasmonic modulators in normal atmosphere up to 15 dBm without degradation over several days. Next steps include further development towards a high-temperature operation in normal atmosphere.

#### 6. References

- [1] C.-J. Chung, et al., J. Lightwave Technol. 36, 1568-1575 (2018).
- [2] M. S. Lebby, in Integrated Photonics Platforms: Fundamental Research,
- Manufacturing and Applications, (International Society for Optics and Photonics, 2020), p. 113640F
- [3] W. Heni, et al., ACS Photonics 4. 1576-1590 (2017).
- [4] R. S. Weis, and T. K. Gaylord, Appl. Phys. A 37, 191-203 (1985)
   [5] C. Kieninger, et al., Optica 5, 739-748 (2018).
- [6] R. Palmer, et al., Lightwave Technology, Journal of 32, 2726-2734 (2014).
- [7] L. R. Dalton, Organic electro-optics and photonics: Molecules, polymers and crystals (Cambridge University Press Cambridge, 2015).
- [8] D. Jin, et al., *EO polymer modulators reliability study* (SPIE, 2010).
  [9] G.-W. Lu, et al., Nat. Commun. 11, 4224 (2020).

- [10] Y. Enami, et al., J. Lightwave Technol. **36**, 4181-4189 (2018).
   [11] A. Melikyan, et al., Nature Photon. **8**, 229-233 (2014).
- [12] B. H. Robinson, et al., J. Lightwave Technol. 36, 5036-5047 (2018).
- [13] H. Xu, et al., Chemistry of Materials 32, 1408-1421 (2020).
   [14] Y. Shuto, and M. Amano, Journal of Applied Physics 77, 4632-4638 (1995).