Electrochemical Optical Actuators: Controlling the Light through Ions

F. Morichetti[1], S. Zanotto[2], A. Blancato[1], F. Berkemeier[3], M. Muñoz Castro[3], A. Buchheit[4], H-D. Wiemhöfer[4], G. Schmitz[5], C. Klitis[6], M. Sorel[6], and A. Melloni[1]

[1]*Dipartimento di Elettronica, Informazione e Bioingegneria, Politecnico di Milano, Italy*

[2]*Istituto Nazionale di Ottica - CNR and LENS, Università di Firenze, Italy*

[3]*Institute of Materials Physics, University of Münster, Germany*

[4]*Institute of Inorganic and Analytical Chemistry, University of Münster, Germany*

[5]*Institute of Materials Science, University of Stuttgart, Germany*

[6]*School of Engineering, University of Glasgow, UK*

e-mail: francesco.morichetti@polimi.it

ABSTRACT

The insertion of mobile ions and coupled changes of electron concentration are exploited to induce a non-volatile and reversible change of the optical properties of mixed ionic and electronic conductors (MIECs). The physical mechanisms responsible for the change of the real and imaginary part of the MIECs' refractive index upon ion-intercalation are extensively investigated in the visible and near-IR range. Applications of the proposed electrochemically driven optical actuators are discussed for the manipulation of the light in an optical chip.

Keywords: tunable photonic devices, optical waveguides, silicon photonics, optical actuators, mixed ionic electronic conductors, metasurfaces.

1. INTRODUCTION

Different physical effects can be exploited to manipulate the properties of an optical medium. For instance, in integrated optics, thermooptic actuators are the most established approach to modify the refractive index of an optical waveguide. However, power consumption and thermal crosstalk are severe limits of this approach towards large scale of integration. In order to reduce power consumption, self-holding actuators, that are reversible switching devices that can maintain the state without the need of "always on" power dissipation, have been recently proposed. Phase Change Materials (PCMs) based on GeSbTe (GST) compounds have been proposed to realize on-chip photonic memory elements, yet requiring an optical control signal to reversibly switch the PCM state across crystalline and amorphous state [1]. Electrically driven intensity actuators have been realized by exploiting insulator–metal phase transition in vanadium dioxide (VO_2) [2] and an electrically induced creation/elimination of a conductive path in a gold/silicon dioxide/indium-tin oxide plasmonic structure has been demonstrated onto a silicon photonic waveguide [3].

In this work, we propose a new mechanism to realize self-holding optical actuators, which is based on the switching properties of mixed ionic electric conductors (MIECs), such as V_2O_5, WO_3, $LiCoO_2$. In MIECs, the local stoichiometry of the material can be modified by electrochemical injection of ions and electrons. Applying an external voltage, the composition of the material can be changed, thus inducing a continuous variation of the optical properties. Advantageously, driving currents are only needed for switching, but not for holding the steady state. In particular we investigate the intensity switching properties of V_2O_5 films in the near infrared range, upon intercalation of lithium ions. An in-depth characterization of the optical properties of Li-intercalated films V_2O_5 films is presented. The possibility to integrate V_2O_5 in Si waveguides is demonstrated, and a proof of concept of the switching mechanism is achieved on a tunable metasurface device.

2. FILM PREPARATION AND CHARACTERIZATION

To assess the switching properties of Li intercalated V_2O_5, thin films were deposited via dc-sputtering using a vanadium metal target, inserting oxygen into the sputter chamber as a reactive component. V_2O_5 layer deposition was performed at room temperature, followed by an annealing at 250°C for 24 hours under ambient conditions. After preparation, the optical properties of the V_2O_5 were modified by changing the lithium concentration. The lithiation/delithiation process, leading to the following compositional change

$$y\,Li^+ + y\,e^- + V_2O_5 \quad \leftrightarrow \quad Li_y\text{-}V_2O_5.$$

was carried out electrochemically, by using a three electrodes setup, as shown in Fig. 1(a). Metallic lithium was used for the reference (RE) and counter (CE) electrode, while the bilayer sample (Pt + V_2O_5) served as working electrode (WE). As for the liquid electrolyte, a 1:1 mixture of dimetylcarbonate and ethylencarbonate was used, containing 1 mol/l $LiClO_4$ as conductive salt. To avoid any kind of oxidation, the whole cell was mounted inside an argon filled glove box. The electrochemical functionality of the V_2O_5 thin films was validated via cyclic voltammetry, confirming the cycling stability of the deposited films.

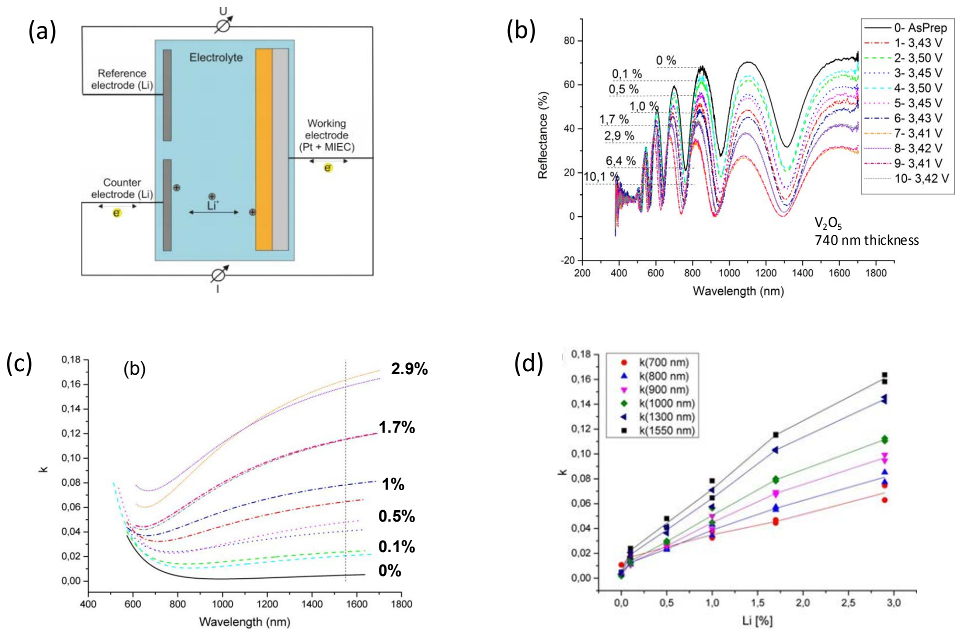

Figure 1: (a) Schematic of the experimental setup to electrochemically change the Li concentration of the V_2O_5 layers; (b) Optical spectra of a 740 nm thin V_2O_5 layer at different Li concentrations; (c) Dispersion relations of the extinction coefficient k; (d) extinction coefficient k at different wavelengths, as a function of the Li content.

The optical properties of the V_2O_5 layers were characterized by optical reflection spectroscopy. A Pt layer of around 100 nm was deposited on a polished Si substrate. On top of the Pt layer, the V_2O_5 layer was deposited, with a thickness of 740 nm. The Li concentration x_{Li} was changed using chronopotentiometry at a current density of 2 µA/cm². After each chronopotentiometric step, the optical response of the films was measured. As shown in Fig. 1(b), the visibility of the fringes varies with x_{Li}, thus demonstrating that different lithiation states result in a self-holding, yet reversible, change in the optical state of the V_2O_5 film. Regarding retention, results indicate that the electrical and optical properties of Li intercalated V_2O_5 are stable over a time scale of at least several days. Figure 1(c), shows the dispersion curves of the imaginary (*k*) part of the refractive index extracted from the reflectance data of Fig. 1(b), assuming a Cauchy model. A strong increase of the material absorption versus Li concentration is observed in the near infrared range. This effect can be attributed to local changes in the valence state of vanadium (from V^{5+} to V^{4+}) due to the intercalation of ions and coupled electrons into the V_2O_5 matrix [4], which result in the creation of small polaron particle absorbing in the near infrared range. Figure 1(d) shows that *k* increases linearly versus Li concentration with a slope that becomes steeper at higher wavelengths. At 1550 nm, the k_0 value of the as-prepared V_2O_5 film is about 5e-3 while the variation of *k* with Li concentration x_{Li} [%] can be approximated by the following linear relation $k = k_0 + \Delta k = 0.005 + 0.052 x_{Li}$.

For an intensity actuator, a figure of merit (FOM) is given by the ratio between the extinction ratio (ER), that is the loss modulation, and the insertion loss in the transparent state (IL_{tr}) [5], that is ultimately related to the absorption properties of the switching material [6]:

$$FOM = \frac{ER}{IL_{tr}} = \frac{\Delta k}{k} = \frac{0.05x}{0.005} = 10x \,. \tag{1}$$

This implies that with a 10% Li concentration, a FOM of about 100 is achievable, leading to ER = 20 dB in a device with IL_{t} = 0.2 dB. This figure is more than one order of magnitude higher than that reached in state-of-the-art integrated self-holding actuators, where a FOM of about 3 [2] and 1 [3] was demonstrated.

3. INTEGRATION of V_2O_5 IN SILICON WAVEGUIDES

A V_2O_5 film was integrated as upper cladding of Si photonic waveguides, after selective removal of the silica upper cladding. The waveguide pattern was defined by electron beam lithography on a 300 nm-thick layer of HSQ; waveguides were then etched in an ICP tool with a C4F8/SF6 gas chemistry. The waveguides were finally cladded by a 800 nm thick bilayer of HSQ and PECVD silica. Selective cladding removal was achieved by exposing and developing a thick layer of PMMA and etching the HSQ/PECVD bilayer with a CHF_3 dry etching chemistry. Partial etching of the HSQ layer resulted in waveguides being still covered by a 50 nm upper cladding, as indicated in the sketch of Fig 2(b). A 600 nm V_2O_5 film of was sputtered on the SOI chip according to the procedure described in Sec. 2. The deposited layers exhibit a uniform surface without cracks and pinholes, as shown by SEM image of Fig. 2(b), and a very good adhesion on the overall substrate. XRD measurements also confirmed the single phase of V_2O_5 (α-phase).

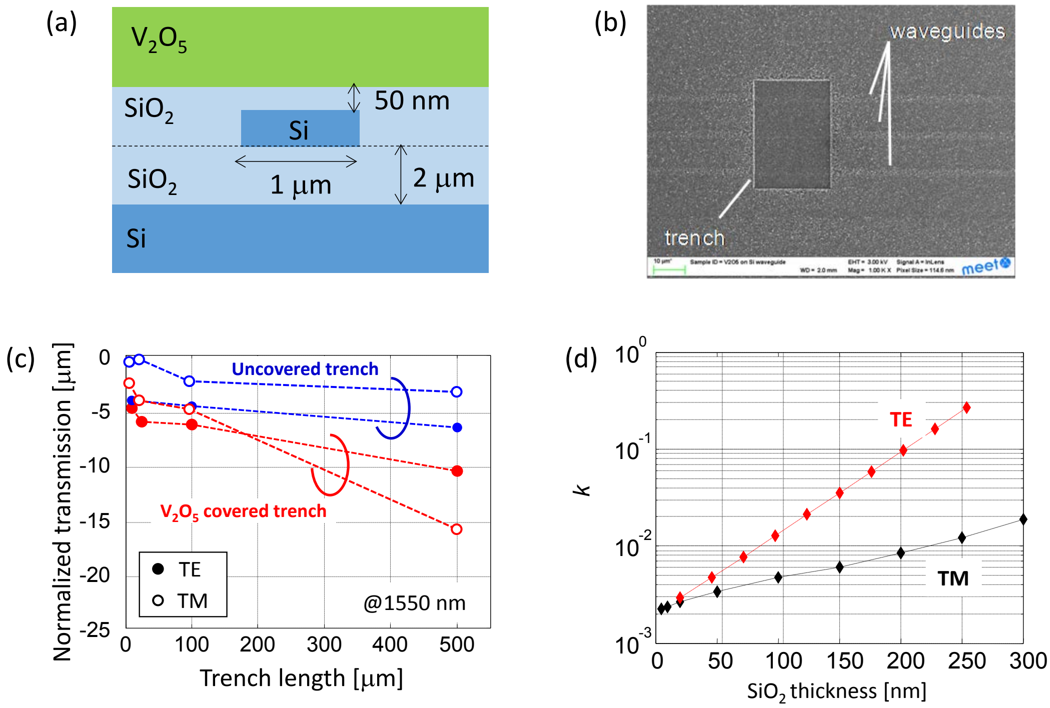

Figure 2: (a) Schematic of the waveguide cross-section inside the trench; (b) SEM picture of the trench region after V_2O_5 deposition; (c) Normalized transmission of 1-µm-wide Si waveguides with uncovered trenches (blue markers) and V_2O_5-covered trenches (red markers) for TE (filled) and TM (void) polarization; (d) Extinction coefficient (k) of the V_2O_5 cladding material extracted from data of (c).

To estimate the impact of the deposited V_2O_5 film deposited, transmission loss measurements were performed on two samples fabricated in the same run; one of the chips was left uncovered (no V_2O_5 film) and was used as a reference, the other was covered with a film of V_2O_5. Frequency domain measurements were carried out, for both TE and TM polarized input light, in the wavelength range from 1520 to 1580 nm. The light was coupled into the Si waveguide using lensed tapered optical fibres with a spot size of 1.7 µm. Results in Fig. 2(c) show the transmitted light, averaged over a 20-nm-wide bandwidth around a wavelength λ = 1550 nm, for TE and TM polarized input light and for an increasing length of the trench section. Blue circles refer to the reference sample, while red circles refer to the V_2O_5 cladded sample. Results indicate that uncovered trenches exhibit losses of 5 dB/mm for both TE and TM polarization. The increase of propagation loss due to the V_2O_5 film is about 10 dB/mm ($\alpha_{wg,TE} = 23$ cm^{-1}) for TE polarization and 30 dB/mm ($\alpha_{wg,TM} = 70$ cm^{-1}) for TM. Assuming a 10 µm long actuator, this would result in an almost negligible loss of the trench itself (0.05 dB) and to an insertion loss of about 0.1 dB for TE polarization and 0.3 dB for TM polarization when covered with V_2O_5.

To extract the loss coefficient of the V_2O_5 material from the waveguide propagation loss, the field confinement factor Γ in the V_2O_5 film was estimated as a function of the thickness of the residual cap layer on top of the Si core. For a cap layer of 50 nm, Γ is about 6% and 25% for TE and TM polarization respectively. Considering the following relation between the waveguide loss α_{wg} and the material loss α_m,,

$$\alpha_{wg} = \Gamma \alpha_m = \frac{4\pi}{\lambda} \Gamma k, \quad (3)$$

a value of k of about 5e-3 is extracted, in agreement with the k values measured on thin films [see Fig. 2(d)].

4. TUNABLE PLASMONIC METASURFACES

In order to have a proof-of-concept validation of a tunable, self-holding reversible devices based on the proposed approach, we designed, fabricated and characterized a plasmonic metasurface that can be tuned by exploiting Li intercalation in a V_2O_5 film.

A schematic representation of the device is given in Fig. 3(a). A 520-nm V_2O_5 film is first sputter-deposited on an optically thick Pt layer, followed by the patterning of arrays of aluminum nanobricks. The size of the individual nanobricks is 255 nm × 510 nm, as in the SEM picture of Fig. 3(b). This feature is optimized to exhibit strong metasurface resonances and consequent linear dichroism. The nanobricks have been realized by means of electron beam lithography followed by physical vapor metal deposition and lift-off.

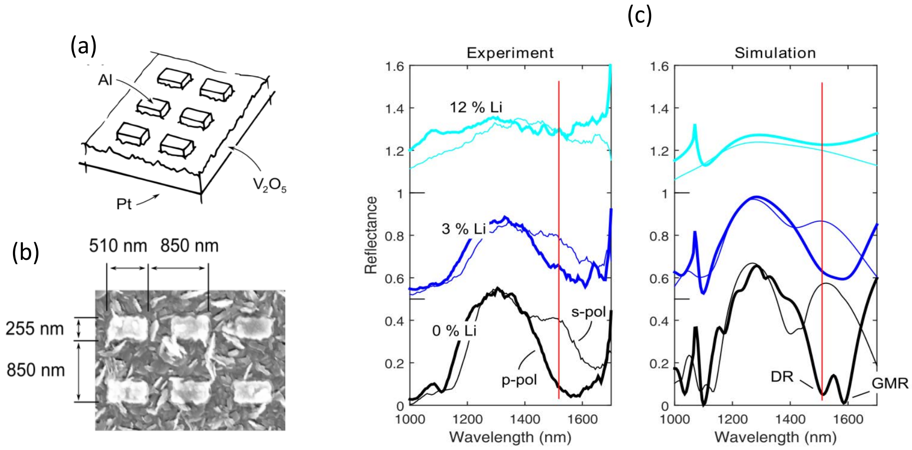

Figure 3: (a) Schematic and (b) SEM picture of the tunable plasmonic metasurface; (c) Metasurface reflectance spectra at different steps of Lithium intercalation. The curves are reported in absolute units, apart from an offset of 0.5 (1) for the 3% (12%) cases, respectively. P-pol indicates that the electric field of the incident wave is parallel to the incidence plane; the latter being defined as the plane orthogonal to the sample surface and parallel to the long axis of the nanobricks. (DR, dipole resonance; GMR, guided mode resonance).

Several electrochemical lithiation/delithiation steps of the V_2O_5 layer were performed with the three electrode setup of Fig. 1(a). Film lithiation/delithiation was carried out via chronopotentiometry at a current load of 2 $\mu A \cdot cm^{-2}$. The Li content was varied stepwise and after each step quasi-normal incidence (15°) reflectance and ellipsometry spectra were acquired, revealing the tuning mechanisms occurring in the metasurface. Figure 3(c) shows the measured reflectance spectra, along with the corresponding simulations. As highlighted by the red vertical line, a strong and tunable linear dichroism is observed at a wavelength slightly above 1520 nm. This dichroism is attributed to the excitation of the dipole resonance (DR) of the nanobricks. In the simulated spectra the p-polarized reflectance at 0% Lithium concentration also presents a second dip, this time attributed to the guided mode resonance (GMR). The resulting double-dip structure, however, was not observed in the experiment, probably as a consequence of the surface roughness which limits the long-range phase coherence required for the onset of a well-resolved GMR. Nevertheless, the V_2O_5-including metasurface fulfilled the proposed goal of demonstrating a functional photonic device, tunable through lithium intercalation in a MIEC.

5. CONCLUSION

We have shown that the optical properties of V_2O_5 films can be modified by electrochemical injection of Li ions. The switching mechanism is fully reversible and inherently self-holding, since a driving current is only needed for switching, but not for keeping the steady state. In the near-IR range, the extinction coefficient of non-intercalated V_2O_5 is sufficiently low ($k = 5\times10^{-3}$) to enable its integration in silicon waveguides for the realization of low-loss, high ER, non-volatile self-holding actuators. Upon Li intercalation, an ER as high as 20 dB can be achieved in devices with transparent state loss of 0.2 dB. The effectiveness of the proposed switching mechanism has been demonstrated by electrochemically tuning the linear dichroism of a plasmonic metasurface.

ACKNOWLEDGEMENTS

The research leading to these results has received funding from the European Union's Seventh Framework Programme BBOI (FP7/2007/2013) under grant agreement no. 323734.

REFERENCES

[1] D. Tanaka *et al.*, "Demonstration of 1000-times switching of phase-change optical gate with Si wire waveguides," *Electronics Letters*, vol. 47, no. 4, Feb. 2011.

[2] A. Joushaghani, B. A. Kruger, S. Paradis, D. Alain, J. S. Aitchison, and J. K. S. Poon, *Appl. Phys. Lett.* 102, 061101 (2013).

[3] C. Hoessbacher, Y. Fedoryshyn, A. Emboras, A. Melikyan, M. Kohl, D. Hillerkuss, C. Hafner, and J. Leuthold, "The plasmonic memristor: A latching optical switch," *Optica* 1, 198-202 (2014).

[4] A. Talledo, A. M. Andersson, and C. G. Granqvist, "Structure and optical absorption of Li y V_2O_5 thin films," *Journal of Applied Physics* 69, 3261 (1991).

[5] B. A. Kruger, A. Joushaghani, and J. K. S. Poon, "Design of electrically driven hybrid vanadium dioxide (VO2) plasmonic switches," *Opt. Express* 20, 23598-23609 (2012).

[6] S. Zanotto, F. Morichetti, and A. Melloni, "Fundamental limits on the losses of phase and amplitude optical actuators," *Laser & Photonics Reviews* 9 (6), 666-673.