Chemically enhanced bacteriorhodopsin thin-film spatial light modulator

Q. Wang Song, Chungping Zhang, and Robert Blumer

W. M. Keck Center for Molecular Electronics and Department of Electrical and Computer Engineering, Syracuse University, Syracuse, New York 13244-1240

Richard B. Gross, Zhongping Chen, and Robert R. Birge

W. M. Keck Center for Molecular Electronics and Department of Chemistry, Syracuse University, Syracuse New York 13244-1240

Received January 8, 1993

An optically addressed spatial light modulator based on a thin film of chemically enhanced bacteriorhodopsin is demonstrated. Incoherent-to-coherent light conversion is achieved by exploitation of both the large shift in absorption maxima accompanying the $bR \rightarrow M$ phototransformation and the extended M-intermediate lifetime resulting from the chemical enhancement of the protein at high pH. The device exhibits a linear dynamic range of 120:1 at 514 nm and a resolution of ~100 line pairs/mm.

Spatial light modulators (SLM's) provide the real-time input–output interfaces and the processing elements fundamental to nearly all optical processing systems.[1] At present, one of the key limitations precluding the widespread implementation of these types of system is the general absence of SLM's that possess high resolution, large space–bandwidth product, long-term stability, adequate speed, and low cost. Most of these shortcomings can be directly attributed to device material limitations. In this Letter we demonstrate an optically addressed SLM based on a thin polymeric film containing bacteriorhodopsin.

Bacteriorhodopsin (BR) is the photochromic protein found in the purple membrane of the bacterium *Halobacterium salinarium*.[2,3] On the absorption of light energy by an internally bound retinyl chromophore, BR undergoes a complex photocycle characterized by several spectroscopically distinct thermal intermediates (see Fig. 1). A number of investigations describing BR's use in optical applications were recently reported.[3–8] The significant feature of this biomaterial derives from the potential of modifying the protein's photochromic properties through chemical enhancement or by genetic manipulation of the native protein. We have focused on chemically enhanced films containing the wild-type protein, diaminopropane, and guanidine hydrochloride in a poly(vinylalcohol) matrix. Compared with a film containing only the native protein at pH ~ 7, the film prepared in this investigation showed a $>10^3$ increase in the M-intermediate lifetime. We fabricated the film by pipetting ~700 μL of a solution (pH > 9) containing concentrated BR, poly(vinylalcohol), guanidine hydrochloride, and diaminopropane onto a glass disk.[9] The cast film was dried for 48 h and subsequently sandwiched between this and another glass disk. The film was of high optical quality over an aperture of 20 mm and exhibited an M-lifetime of 7 s. The optical density of the film, measured at 570 nm, was ~5.4, and the film thickness was ~200 μm.

The two important photochemical states in the BR photocycle relevant to this investigation are referred to as bR and M. bR represents the ground state, characterized by a strong absorption in the green-yellow region of the visible spectrum ($\lambda_{max} = 568$ nm). M denotes the longest-lived thermal intermediate in the photocycle and exhibits a strongly blue-shifted absorption spectrum ($\lambda_{max} = 412$ nm) relative to the ground state. Figure 2 shows the experimentally determined absorbance spectrum for each state in the BR film. Since the M intermediate has a significantly longer lifetime than all other thermal intermediates in the protein photocycle, the photocycle can be simplified to a two-state photochromic system:

$$bR(\text{State 0}) \underset{\Phi_2 \sim 0.65}{\overset{\Phi_1 \sim 0.65}{\rightleftharpoons}} M(\text{State 1}),$$

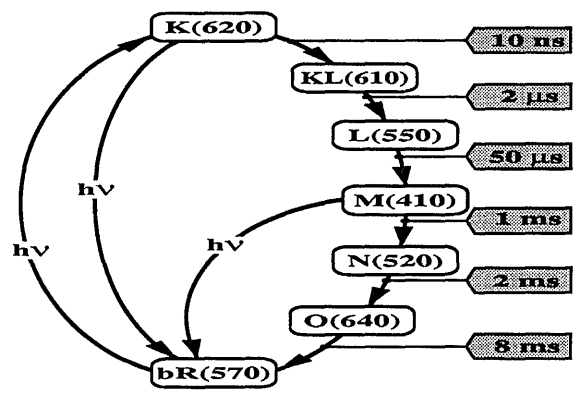


Fig. 1. Schematic diagram of the photochemical and thermal reactions in the BR photocycle. The thermal intermediates are denoted by letters. The numbers in parentheses indicate the wavelength of the absorption maximum for each intermediate state. The numbers in shaded boxes show the formation time of the thermal intermediates.

0146-9592/93/161373-03$6.00/0

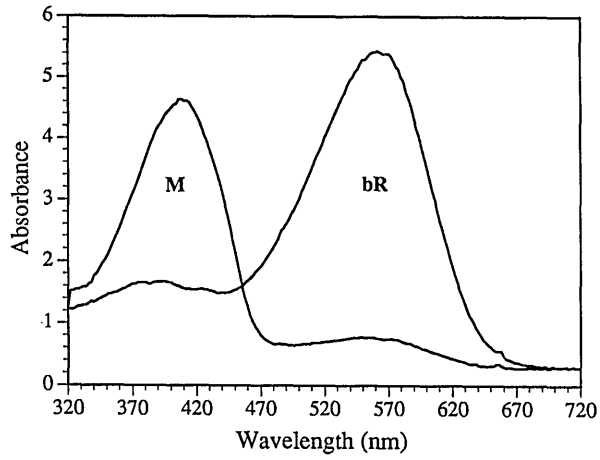


Fig. 2. Measured absorption spectra of the bR and M states in the chemically enhanced film. The addition of the chemicals guanidine hydrochloride and diaminopropane caused no absorption maxima shifts relative to that of the native protein containing no chemicals.

where Φ_1 and Φ_2 represent the forward and reverse quantum yields,[10] respectively.

The light-transmission properties of the film can be analyzed with the scheme shown above. The differential equation describing the rate of change of the concentration of bR is

$$\frac{\mathrm{d}[bR]}{\mathrm{d}t} = \sum_{i=1}^{\text{all wavelengths}} -K_{\lambda_i}^{bR\Rightarrow M}[bR] + K_{\lambda_i}^{M\Rightarrow bR}[M] + k_M[M], \quad (1)$$

where $[bR]$ and $[M]$ are the molar concentrations of bR and M, respectively, k_M is the M-intermediate thermal decay rate, and $K_{\lambda_i}^{bR\Rightarrow M}$ and $K_{\lambda_i}^{M\Rightarrow bR}$ are the forward and reverse phenomenological rate constants, respectively, given by

$$K_{\lambda_i} = \frac{2.3026\Phi\epsilon(\lambda_i)\lambda_i I(\lambda_i)}{N_a hc}, \quad (2)$$

where Φ is the quantum yield for the forward (or reverse) photoreaction. $\epsilon(\lambda)$ is the corresponding molar extinction coefficient for the photoreaction considered, $I(\lambda)$ is the illumination intensity (mW/cm^2), N_a is Avogadro's number, h is Planck's constant, and c is the speed of light. The fraction of $[bR]$ under the steady-state illumination can be written as

$$\frac{[bR]}{[bR_0]} = \sum_{i}^{\text{all wavelengths}} \frac{K_{\lambda_i}^{M\Rightarrow bR} + k_m}{K_{\lambda_i}^{bR\Rightarrow M} + K_{\lambda_i}^{M\Rightarrow bR} + k_m}, \quad (3)$$

where $[bR_0]$ is the total molar concentration of bR before illumination ($[bR] + [M] = [bR_0]$). Equation (3) is valid for an optically thin layer of absorbing material for which the transmitted intensity is adequately described by the Beer–Lambert law. The recursive relation describing the intensity transmitted through the nth layer (I_n) is found by substitution of Eq. (3) into the Beer–Lambert law of absorption[9]:

$$I_n = I_{(n-1)}\exp(-2.3026\{\epsilon_M(\lambda)[bR_0] + \{\epsilon_{bR}(\lambda) - \epsilon_M(\lambda)\}\{[bR]/[bR_0]\}_n[bR_0]\}d_n), \quad (4)$$

where d_n is the thickness, in centimeters, of the nth layer and the remaining variables were defined previously. The assumed values for the various parameters in the simulation were taken to be thickness 200 μm, $\lambda_i = 514$ nm, $\Phi_{bR\Rightarrow M} = \Phi_{M\Rightarrow bR} = 0.65$, $\epsilon_{bR}^{514} = 42{,}000$, $\epsilon_M^{514} = 0$, O.D.$_{514} = 5.4$, and $k_M = 1/7$ s^{-1} ($\tau_M = 1/k_M = 7$ s). By dividing the film thickness into 200 thin layers ($d_n = 1$ μm) and numerically integrating Eq. (4), we obtained the intensity dependent transmission characteristics of the thin film at 514 nm. The results are shown in Fig. 3.

The principle of the optically addressed BR SLM follows from the discussion above. The transmittance of a weak coherent readout beam is controlled by an incoherent light distribution containing the input information. For example, at a readout light wavelength of 514 nm the minimum transmittance of the film can be predicted from the absorption spectra given in Fig. 2 as $T_{\min} \sim 10^{-3.7}$. On the application of the incoherent write beam, $bR \rightarrow M$ photochemistry blue shifts the absorption band of the illuminated regions of the BR film. The maximum transmittance for the reading light is now given by $T_{\max} = 10^{-0.6}$, after nearly complete conversion of bR to M. Thus the transmittance of the film to the reading light is controlled by the write-beam intensity. The dynamic range of the film transmittance at 514 nm, which we define as $T_{\max}/T_{\min}$, is estimated to be $\sim 10^3$. The dynamic range is expected to improve to $>10^4$ if readout is performed at the absorption maximum of bR.

The experimental setup used for characterizing the transmission properties of the BR SLM is shown in Fig. 4. An input transparency, illuminated by a tungsten white-light source, is imaged onto the BR film by lens L1. A bandpass filter (400–800 nm) selects only the visible portion of the spectrum emitted from the lamp. The 514-nm line from an argon-ion laser serves as the source of coherent readout. A narrow-band interference filter eliminates the transmitted white light. The combination of a polarizing beam splitter and a

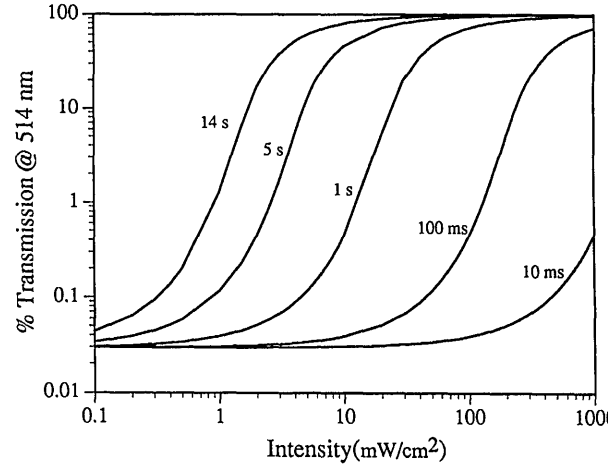


Fig. 3. Results of computer simulations predicting the intensity-controlled transmission properties of a BR film. Each curve is calculated for a specific M-intermediate lifetime (see the inset numbers). The film O.D.$_{514}$ was assumed to be 3.7 and the film thickness 200 μm.

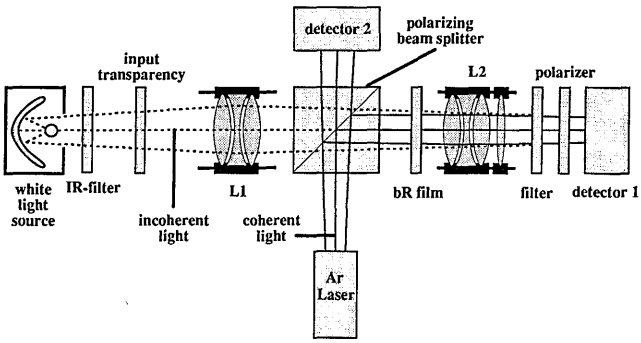


Fig. 4. Schematic diagram of the experimental apparatus used for measuring the dynamic range and resolution of the BR SLM.

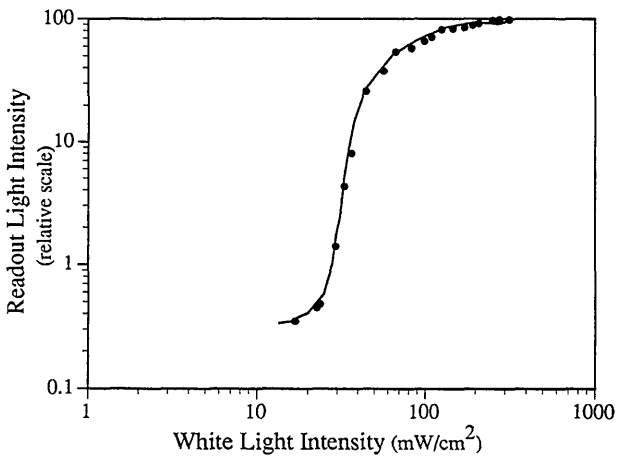
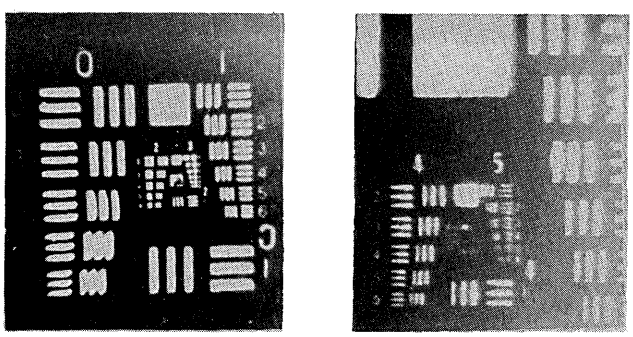


Fig. 5. Relative transmission of a weak coherent readout beam (514 nm) as a function of incoherent white-light intensity measured from the BR SLM. The intensity of the readout beam was 0.16 mW/cm^2.



(a) (b)

Fig. 6. Photographs of the reduced (0.4×) resolution chart taken after readout from the BR SLM: (a) the entire resolution chart, (b) an enlarged central portion of chart. The resolution of the film was found to be ~100 line pairs/mm after correction for demagnification.

polarizer further excludes extraneous white light within the bandwidth of the interference filter such that only coherent laser light is detected at the output plane. Detectors 1 and 2 are used to monitor the intensities of the reading and writing lights, respectively. The low intensity of the readout beam permitted nondestructive coherent readout of the image. Figure 5 shows the film's transmission response as a function of white-light intensity for a 5 mm × 5 mm input aperture. It can be seen from the curve that a dynamic range of ~200 is achieved. This result is consistent with the prediction from the absorbance measurements given in Fig. 2.

We measured the resolution of the BR SLM by placing a U.S. Air Force resolution chart in the input plane of Fig. 3. An additional lens, L2, placed behind the film, was used to image the pattern into the film plane of a 35-mm camera. Because of the small numerical aperture of the imaging lenses, the image of the resolution chart was demagnified to 1/2.5 of its original size. Figure 6 shows a picture of the chart image readout from the device. The highest resolvable group was found to be group 5, element 3, which corresponds to a resolution of 100 line pairs/mm after correction for image demagnification. The measured resolution was found to be limited by the resolution of the imaging lenses, which were ordinary 35-mm camera lenses. The intrinsic resolution of the BR film is known to exceed 2000 line pairs/mm.[11] The space–bandwidth product (number of resolvable pixels) of the device was calculated to be ~10^6. The write speed was found to be proportional to the intensity of the write light and ranged from several seconds, at moderate write intensities, to hundreds of milliseconds at maximum intensities.

In summary, we have demonstrated an optically addressed spatial light modulator based on a thin film containing chemically enhanced bacteriorhodopsin. The notable features of the device include structural simplicity, large space–bandwidth product, low cost, and no need for an electrical control circuit.

We acknowledge the support of the W. M. Keck Foundation and of the U.S. Air Force under contracts F30602-91-C-0084 and F30602-92-C-0036.

References

1. J. A. Neff, R. A. Athale, and S. H. Lee, Proc. IEEE **78,** 826 (1990).
2. R. R. Birge, Annu. Rev. Phys. Chem. **41,** 683 (1990).
3. D. Oesterhelt, C. Brauchle, and N. Hampp, Q. Rev. Biophys. **24,** 425 (1991).
4. R. Thoma, N. Hampp, C. Bräuchle, and D. Oesterhelt, Opt. Lett. **16,** 651 (1991).
5. O. Werner, B. Fisher, A. Lewis, and I. Nebenzahl, Opt. Lett. **15,** 1117 (1990).
6. Z. Chen, A. Lewis, H. Takei, and I. Nabenzahl, Appl. Opt. **30,** 5188 (1991).
7. N. N. Vsevolodov, G. R. Ivanitskii, M. S. Soskin, and V. B. Taranenko, Avtometrya **2,** 41 (1986).
8. Q. W. Song, Z. Chen, P. Blumer, R. Gross, Z. Chen, and R. Birge, Opt. Lett. **18,** 775 (1993).
9. R. B. Gross, K. C. Izgi, and R. R. Birge, Proc. Soc. Photo-Opt. Instrum. Eng. **1662,** 186 (1992).
10. B. Becher and T. G. Ebrey, Biophys. J. **17,** 185 (1977).
11. N. Hampp, A. Popp, C. Bräuchle, and D. Oesterhelt, J. Phys. Chem. **96,** 4679 (1992).