Two-stage optical recording: photoinduced birefringence and surface-mediated bits storage in bisazo-containing copolymers towards ultrahigh data memory

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Abstract: Ultrahigh density data storage is in high demand in the current age of big data and thus motivates many innovative storage technologies. Femtosecond laser induced multi-dimensional optical data storage is an appealing method to fulfill the demand of ultrahigh storage capacity. Here we report a femtosecond laser induced two-stage optical storage in bisazo benzene copolymer films by manipulating the recording energies. Different mechanisms can be selected for specified memory use: two-photon isomerization (TPI) and laser induced surface deformation. Giant birefringence can be generated by TPI and brings about high signal-to-noise ratio (>20 dB) multi-dimensional reversible storage. Polarization-dependent surface deformation arises when increasing the recording energy, which not only facilitates the multi-level storage by black bits (dots), but also enhances the bits’ readout signal and storing stability. This facile bits recording method, which enables completely different recording mechanisms in an identical storage medium, paves the way for sustainable big data storage.

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References and links
1. Introduction

As vast amount of information is newly generated every day in the fields of economics, education, health, business, and so on [1, 2], it becomes extremely challenging to store such amount of data by using our current information storage technologies. Although big data cloud storage center has been heralded as a promising solution in future, the fundamental storage devices are still unsatisfactory to meet the requirement of massive information on petabyte or exabyte scale. Furthermore, the magnetic or electric storage devices consume large amount of energy even when the mediums are in the idle status. In addition, the limited lifetime of the current storage technologies results in great energy waste because of frequent data migration and hardware update. Comparatively, optical data storage features high reliability, energy conservation and sustainability. However, optical storage is rarely used in big data centers because of its unfavorable storage capacity restricted by the light diffraction limit. Consequently, a variety of novel approaches such as multi-dimensional storage [3–5], super-resolution recording [6–8], and holographic recording [9–11], have emerged aiming to further increase the optical storage capacity.

Multi-dimensional storage, in which other physical dimensions are integrated inside the identical domain of recording medium, is regarded to be a superior approach for capacity improvement. It is able to increase the storage capacity by orders of magnitude without changing the recording wavelength and numerical aperture of objective [12]. Therefore, the existing optical storage technologies can be readily updated with minor changes to their...
optical system and mechanical configuration. Up to now, spatially multi-layer [4], recording wavelength [3, 13], polarization [5, 12] and bits gray-level [5, 14–16] have been successfully exploited as the extra-dimension of data recording, enabling the storage capacity to the order of terabytes per disc. However, previous studies concern themselves with a single optical property change of the recorded materials, e.g. birefringence [5] or photobleaching [14]. So far there are no reports on the finding that different types of storage can be carried out in the same film by a single laser. Moreover, the poor signal-to-noise ratio (SNR) of the multiplexed data seriously limits the practical application of multi-dimensional storage techniques. Here, we report a two-stage optical recording strategy in photoisomeric polymer by femtosecond laser. In the first stage, recording and retrieving of multi-dimensional data with high SNR is demonstrated. In the second stage, the accompanying surface profile of the recorded bits is investigated and explicated by the electric field force induced mass migration. The surface-mediated data recording is thought to be able to enhance the bits signal intensity and based on which, quasi-permanent multi-gray level storage is demonstrated.

2. Bits recording by photoinduced birefringence

Figure 1(a) illustrates the experimental setup for polarization recording and reading. A polarizer (P1) is used to control the incident laser polarization for recording. A Ti:sapphire femtosecond laser (Chameleon Vision-S, Coherent) is employed for bits recording with a central wavelength of 800 nm, a pulse duration of 75 fs and a repetition rate of 80 MHz [17]. White light from a halogen lamp is used as reading beam, with a polarizer P2 for regulating the reading polarization. The white light with a low intensity is superior to other laser beams acting as the reading light because it causes negligible secondary treatment to the medium. There is another polarizer P3 between the back aperture of objective and CCD detector, whose optical axis is perpendicular to that of P1. Both the sample and polarizers are able to be rotated, as depicted in Fig. 1(b). A bisazobenzene polymer, named by poly(HEMA-co-M2BAN) is used as recording material. Hydroxyethyl methacrylate (HEMA) is used to synthesize the copolymer to improve the film hydrophilicity and help to prepare films with good homogeneity. And the interface compatibility between bisazobenzene functional layer and polyvinyl alcohol (PVA) is improved in order to form thick multilayer film. Compared with other monoazo-polymers, bisazobenzene chromophore contains two conjoining azo bonds, and has been proved to possess stronger photoinduced anisotropy due to the longer –N=N- chain and resultant longer transition dipole moment [18–20]. In order to match the numerical aperture (NA) of the lens in current DVD drive, we use a 40 × microscope objective with a relatively low NA of 0.65 for recording. A mechanical shutter and a combination of half-wave plate and polarizer is utilized to determine the exposure time and recording laser power. For polarization multiplexing data storage, polarization purity is very critical for the recording and reading performance. The objective with low NA avoids the depolarization effect and the polarization is mostly along the desired direction in the focal field.
Birefringence can be induced in azo-containing polymers by femtosecond laser due to the photoinduced anisotropy of chromophores. The trans isomers are reoriented to be perpendicular to the polarization of recording beam through intermediate unstable cis isomers. In comparison with the similar derivatives containing azobenzene chromophores, bisazobenzene undergoes a relatively complicated trans-cis-trans process which involves intermediate trans-cis and cis-cis states. Different linearly polarized lights propagating through the bits area of recording medium will experience different refractive indices, i.e., $n_o$ and $n_e$, for ordinary ray and extraordinary ray, respectively. A phase difference is generated after passing through the bits region: $\delta = \frac{2\pi d (n_e - n_o)}{\lambda}$, where $d$ is the thickness of the polymer film, $\lambda$ is the wavelength of the incident beam, and $n_e-n_o$ corresponds to the magnitude of birefringence $\Delta n$. Hence the transmission intensity of the reading beam behind the polarizer $P_2$ can be expressed as:

$$I_{out} = I_{in} \sin^2 (2\theta) \sin^2 (\delta/2)$$  \hspace{1cm} (1)$$

where $I_{in}$ is the incident light intensity, $\theta$ is the angle between polarization direction of $P_1$ and optical axis of the recording medium (perpendicular to the recording polarization), as shown in Fig. 1(b). Figure 1(c) shows the readout results when the sample is successively rotated with an interval of $45^\circ$. It can be seen that the recorded bits can be read out only at the angles of $45^\circ$, $135^\circ$, $225^\circ$ and $315^\circ$, whereas no bits can be distinguished when the optical axis of recording medium is along or orthogonal to the polarization direction of $P_1$. This clearly verifies the $\sin^2(2\theta)$ dependence of the reading intensity as implied in Eq. (1). Since the optical axis of the recording medium is perpendicular to the recording beam polarization, the reading beams with polarization parallel or perpendicular to that of recording beam can be regarded as propagating in a homogenous material as if there was no birefringence involved. That is why the bits merge unobtrusively into the background.
3. Multi-dimensional data storage

Based on the exceptional angular dependence of the readout signal as described in the above section, two different bits of information can be encoded in the same region of the recording medium by separating the recording polarizations with an angle of 45°, as demonstrated in Figs. 2(a-d). Letters “F” and “T” are recorded in the first layer by applying 0° and 45° recording polarizations, respectively. Another two letters, “H” and “E”, are recorded in the second layer 25 μm beneath the first one using the same recording strategy. The data is read out when the polarizations of reading beams are 45° to the corresponding recording beams, which further confirms that the birefringence has been induced via two-photon trans-cis-trans process and the optical axis of irradiated bisazobenzene polymer is orientated perpendicular to the polarization of recording beam. The readout bits exhibit a high SNR, with insignificant crosstalk between information from different layers and polarizations. It can be further manifested quantitatively from the line plot of intensity in Figs. 2(e-f). Sharp bits intensity peaks are detected with a SNR higher than 20 dB. In comparison with similar derivatives containing azobenzene chromophores with only one azo bond [21], the high SNR is attributed to the giant birefringence caused by the two alternated azo bonds between three benzene rings in the bisazobenzene copolymer. It is worth mentioning that reading beam or out-of-focus writing beam propagating through an array of birefringent bits will incur a phase aberration and the large birefringence that gives the high SNR will thus be a penalty for multilayer storage [22], which can be resolved by confocal reading configuration or other depth sectioning methods borrowed from microscopy and is beyond the scope of this paper. Moreover, the demonstrated birefringence data recording is reversible. The recorded bits can be erased by circularly polarized femtosecond laser, and then the film can be treated as a fresh medium ready for more recording circles.

![Fig. 2. (a-d) Demonstration of four-dimensional bits storage. (a) and (b) are recorded in the same region of the first layer with 0° and 45° angular polarizations, respectively. (c) and (d) are recorded in the second layer. The interval between neighboring bits is 4 μm. Reading beams with corresponding polarizations are used. Pseudo-colors are used to indicate different layers. (e) and (f) are the line plot of the normalized bits intensity along the dashed lines for the first and the second layer, respectively. Four-dimensional data storage with more layers can be achieved using the polarization-multiplexing technique.](image-url)
4. Photoinduced surface deformation

When the recording dosage (either exposure time or recording power) is increased above a critical threshold, polarization-dependent deformation will be formed on the surface of the material [23, 24]. Different from the thermal ablation by other laser types, the surface deformation caused by femtosecond laser is generally ascribed to the electric field force driven large-scale migration of polymer molecules. According to the point spread function (PSF) of an objective, the optical intensities of the focal spots for planar laser beams with linear and circular polarizations are identical in circular shape with approximately Gaussian-like distribution. Comparatively, the electric field distribution is different for linear and circular polarizations [Fig. 3(a)]. If the surface profile caused by laser is associated with thermal ablation, the shape of holes should depend on the intensity of the focal spot and hence be circular for both linearly and circularly polarized beam irradiations. However, experimental results reveal that the surface deformations are quite different in the two cases: the shape is circular for circular polarization and ellipse for linear polarization, as shown in the 3D surface morphology measured by an atomic force microscope (AFM) [insets of Figs. 3(b)-3(e)]. Therefore, the possible mechanism of thermal ablation is excluded and optical field gradient force, directly related with the magnitude of electric field, arises to be a reasonable origin of the exterior structure formation.

Fig. 3. (a) Optical electrical field distribution calculated for focused linearly and circularly polarized lasers inside the polymer. LP_Ex and LP_Ey are the components of electric field distribution in the directions along and perpendicular to the linear polarization, respectively. CP_Ex and CP_Ey are the components of electric field in two orthogonal directions for circularly polarized light. (b-e) Surface profiles of the bits recorded by femtosecond lasers with circular and linear polarization, respectively. Insets show the three-dimensional topology measured by AFM.
Optical field gradient force model was firstly proposed to explicate the formation of surface-relief gratings (SRGs) fabrication in azo-functionalized materials [23], which is quite similar to the case of surface deformation during bits recording. For plane Gaussian beam with linear polarization, the electric field vector in the focal plane can be derived by vectorial diffraction theory:

\[
\mathbf{E} = \begin{bmatrix} E_x \\ E_y \end{bmatrix} = iC \int_a \left[ \sin(\theta) a(\theta, \phi) \sqrt{\cos(\theta)} \right] \exp \left( ikr \left( z + r \sin(\phi - \varphi) \right) \right) d\theta d\varphi
\]

where \( C \) is the normalized constant, \( a(\theta, \phi) \) is the amplitude distribution of the input light, \( k \) is the wavenumber and \( n \) is the refractive index of the medium. Optical electric field \( \mathbf{E} \) induces a medium polarization \( \mathbf{P} \). For two-photon process, \( \mathbf{P} = \epsilon_0 \chi_3 \mathbf{E} \mathbf{e} \), where \( \epsilon_0 \) is the permittivity of vacuum, \( \chi_3 \) is the third-order nonlinear susceptibility of the medium and \( \mathbf{e} \) is the unit vector of the optical electric field. The force density exerted on azo molecules in a small volume can be expressed by:

\[
f = \nabla \cdot (\mathbf{P} \cdot \mathbf{V} \mathbf{E})
\]

From the equation we can know that the driving force is produced by light electric field and its gradient.

From the measured surface profile we can see that the deformations are almost the same along each directions for a circularly polarized laser irradiation, whereas for the linear polarization recording, the width in the direction parallel to the recording polarization is obviously larger than the transverse direction. That is because the longitudinal component of electric field (i.e. along polarization) is much larger than the other one, thus yielding stronger medium polarization and electric field gradient force. For circular polarization recording, the electric field gradient forces are the same along all the directions, therefore symmetric circular patterns are generated. It is also worth mentioning that the nonthermal property of femtosecond pulsed laser processing enables higher recording speed compared to other newly emerging storage techniques, e.g. heat-assisted magnetic recording (HAMR) [25, 26].

5. Surface-mediated bits recording

In order to investigate the surface-mediated recording effect, a pattern is recorded by using two orthogonal recording polarizations. The recording polarizations are indicated by arrows in Fig. 4(a). The recording power is 40 mW and the exposure time is 300 ms. A white light interferometry optical profiler is used to measure the large-area surface profile [Fig. 4(b)]. It is shown that surface deformations with ellipse shape are obtained and the directions of their long axes are along the recording polarization. It has been reported that the bits carrying photoinduced birefringence can also be read out with an individual linearly polarized beam [5]. From the readout images in Figs. 4(c) and 4(d), it is intriguing that completely different bits are read out for different recording polarizations. The bits appear to be bright when the reading polarization is parallel to that of recording beam, and appear to be dark when the reading polarization is perpendicular to the recording polarization. Moreover, when rotating the reading polarization, the bits intensities smoothly transit from one state to the other (see Visualization 1).
Fig. 4. (a) Mapping of the recording polarizations for a pattern and (b) the corresponding laser-induced surface deformation. Scale bar: 5 μm. The readout results are shown with different reading beams with (c) horizontal and (d) vertical polarizations. Scale bar: 5 μm.

The high gray-scale difference between bright and dark can be attributed to the appearance of the surface deformation. It is known that the data storage based on photoinduced birefringence is derived from the phase modulation of reading beam by the recorded medium. The surface profile with the depth less than the wavelength of reading light will further enhance the phase modulation and give rise to improved bits intensity and gray-level range. Multi-gray-scale optical data storage has been accomplished in photobleaching polymers and glass materials by varying the discrete intensities of the writing beam [14, 27]. In comparison, the surface-mediated storage which can show opposite scales undoubtedly provides much more range for gray-scale encoding, i.e., more levels between positive and negative values are expected to be recorded and discerned using this method. Moreover, control of recording polarization can be used instead of adjustment of recording intensity, which makes the storage system more compact and easier to manipulate in comparison with other multi-gray-scale recordings. Meanwhile, optical data storage with ultra-long lifetime is highly desired for future big data storage. Unlike the photoinduced chemical reactions and optical changes such as photobleaching or birefringence, permanent physical changes of materials like voids and inscription in polymer or glass are considered to be unlimited lifetime recording [27, 28], and have been proven to be stable over centuries. Therefore, the surface-mediated data recording ought to have better stability over a long time scale.

Together with the previous results we have achieved [29], the bits recording can be classified according to the writing dosage into different stages including photoinduced birefringence polarization-multiplexed bits recording, rewritable multi-dimensional bits recording and surface-mediated multi-level bits recording as demonstrated here.

Recording parameters are crucial for the optimal storage capacity, thus are systematically studied here. Different exposure time and recording power are used for bits recording. The measured bits sizes are shown in Fig. 5. When we gradually increase the exposure time, the bits sizes increase rapidly at the early stage and then approach the saturation. Similarly, the bits sizes increase with the recording power. It is found that the appearance of surface deformation does not bring about any change of the readout bits size. In other words, the bits size increases in a regular and harmonious way, which indicates that the surface deformation only affect the bits intensity, not the bits size. Owning to the nonlinear two-photon absorption threshold effect, the minimum size of bits can be achieved at a low recording power (< 4 mW), but the readout bit is not steady because of the power fluctuations of the laser. A stable bit size of ~700 nm (full width at half maximum, FWHM value of bits intensity) can be obtained at a recording power of 6 mW with the objective with NA = 0.65. This value is near the observation resolution of the optical microscope and therefore is close to the limitation of optical readout. Considering the minimum bit size, layer separation and the effect of polarization-multiplexing and multi-gray-scale, the proposed storage method has the ability to
achieve a storage density over 300 Gb/cm$^3$. Smaller bit spots can be anticipated with higher NA objective but new readout setup should be developed. Therefore, by optimizing the recording parameters and integrating multi-gray-scale and polarization multiplexing, a storage capacity of ~TB/disc can be expected.

![Fig. 5. Bits size dependence on (a) exposure time and (b) recording power. Constant laser power of 15 mW and exposure time of 200 ms are used respectively for (a) and (b). Microscopic objectives with different magnification and NA can be chosen for bits reading. Inset of (b) shows an individual bit and its intensity distribution.](image)

6. Discussion and conclusion

We have demonstrated that two recording mechanisms: photoinduced birefringence and surface-mediated data recording, can be applied in the same polymer film. The two recording stages have different features and merits. The first stage recording enables high-SNR four-dimensional storage from which different information can be encoded in the same layer by selecting the recording polarization. Moreover, data storage at this stage is erasable and rewritable. The second stage recording involves surface deformation caused by optical field gradient force, and results in long-term multilevel data storage. This two stage recording strategy in the same medium allows us to select the recording types flexibly according to the practical necessity without changing the optical disc. For instance, the first-stage recording can be selected when the information needs to be manipulated and updated frequently, and the second-stage recording is more suitable for long-term data memory in the optical disc. Furthermore, as a common material for disc production, azo-containing copolymers have evident advantages of low cost, thermal stability and enhanced optical properties, and therefore the proposed two-stage recording technique is more likely to be commercialized.

In summary, we present a two-stage recording strategy: photoinduced birefringence and surface-mediated data recording, in photoisomeric polymer. High-SNR multi-layer polarization-multiplexed bits are recorded by a polarized femtosecond laser with relatively low power. With increased recording power, surface deformations are found to be dependent on the incident polarization and be able to enhance the bits intensity, thus multi-gray-scaled bits recording can be achieved. Finally, experimental parameters are systematically investigated for exploiting the optimal storage capacity. Two different mechanisms are demonstrated in an identical polymer film, which provide us a flexible way for next-generation big data storage.

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