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Article

Application of Photo-Induced Chirality in Covert Authentication

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Featured Application: Photo-induced chirality in thin films of $Ge_2Sb_2Te_5$ can be used to store covert information with application in authentication labels. This information can be revealed by a suitable simple reading device.

Abstract: A new technology to write and read covert information in authentication labels is described. This technology uses the phenomenon of photo-induced chirality in $Ge_2Sb_2Te_5$ thin films to encode the left- or right-circular or linear polarization of the laser beam used to write the label. The written polarization can be revealed by a simple reading device, which is demonstrated to provide the same qualitative information as reading based on cyclotron circular dichroism spectroscopy and imaging. The suggested method, while based on existing manufacturing approaches, offers a balance between technological complexity for writing and simplicity for reading, and may be advantageous as a new authentication technology.

Keywords: authentication labels; chirality; polarization; circular dichroism

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1. Introduction

Authentication labels play an important role in the modern economy. They can commonly be seen, for example, on bank notes and passports. These labels are one of the tested approaches to prevent counterfeiting, which affects about 3% of World Trade [1]. In addition, counterfeiting notably impacts the health and safety of the global community. For example, counterfeit pharmaceuticals or chemical fertilizers pose direct and indirect health risks. Poor-quality counterfeit electrical or electronic components and materials also represent direct and indirect hazards when used in the manufacturing processes of critical products.

Established technologies that underpin current authentication labels are generally based on diffraction grating (so-called optically variable devices, OVDs) and holography concepts.

This technology has evolved incrementally, and hence, there is a growing need to introduce new technological solutions for security labels that are both cheaper and more difficult to reproduce.

The manufacturing of usual OVDs or holographic labels generally requires preparation of an imprint matrix using e-beam lithography, or direct laser writing to prepare the grating arrays. In the latter approach, two-beam interference patterning is used to generate gratings directly on PET substrates that can be used as security labels. The stored images can then be visualized by illumination with a coherent light source [2].

New technologies for use in authentication labels are required and are constantly being proposed, each with corresponding advantages and disadvantages. For example, it has been suggested that unclonable security labels can be printed using ink-jet technology with different quantum dots that emit red, green and blue light to achieve full-color fluorescence in flower-like patterns. These labels can then be read with the help of artificial intelligence [3].

One of the approaches to increasing label security is to store covert information with higher levels of sophistication. As an example, it has been shown that current two-dimensional surface-enhanced Raman scattering (SERS)-based security labels can be extended to three dimensions. The reported 3D pillar microstructures allowed encoding for at least three layers of information within the same area along an axis perpendicular to the plane. These layers can represent predesigned covert images which can only be fully recovered by SERS imaging at predetermined depths [4]. This approach, however, requires complicated equipment to read the labels.

Using polarization of light to encode covert information in security labels is a promising option. Recently, a liquid crystal (LC)-based optical device has been demonstrated, which can selectively reveal images by using polarized illumination. This device consisted of a surface fabricated from patterns of helical photonic crystals of different chirality that encode two different images. The LC layer on top acted as a tunable phase retarder, and by applying a suitable voltage across the LC layer, either a right- or left-circular polarization image could be viewed [5].

Another approach to utilizing circularly polarized light in security labels has been reported using a double-layer arc as 3D chiral color pixels. By varying the arc lengths, a range of colors can be achieved, which differ for left- or right-handed circularly polarized light (CPL). This can be used to produce images with varying intensity and different colors when the label is illuminated by differently handed circularly polarized light [6]. A drawback to this approach is that it requires expensive lithography technology to prepare chiral arc arrays that constitute the chiral pixels.

Assembling luminescent quantum dots in a helical array within a matrix of suitable LC with a chiral dopant presents the possibility of preparing circularly polarized luminescence materials. These materials can be part of a multimodal-responsive security materials that can show responses to light activation, light polarization, temperature, voltage, pressure and viewing angle. The preparation of such materials requires high-quality quantum dots and relies on a multistage synthetic route [7].

One of the other recent suggestions involves combining long afterglow (a phenomenon where energy stored by light irradiation of a luminescent material is slowly released) with CPL, resulting in a circularly polarized long afterglow (CPLA). The synthesis of materials with such properties involves combining an LC membrane with an appropriate luminescent phosphor film in a cementation coupling. To reveal the encoded information, long excitation times (up to 10 min) with UV light may be required [8].

We report here a new concept and straightforward technology based on the phenomenon of photo-induced optical activity in chalcogenide glasses [9,10] for security labeling. This provides an additional covert level of security encoded as the chirality of light used to write the security label and can be integrated with existing security label technologies.

2. Materials and Methods

Thin-film deposition: To demonstrate the application of chirality in covert authentication labels, pure $Ge_2Sb_2Te_5$ (GST) amorphous film 55 ± 3 nm thick (as measured by depth profilometry) was deposited by magnetron radio frequency (RF) sputtering using a commercially sourced GST sputter target (Kurt J. Lesker Company, Clairton, PA, USA) in an argon atmosphere on a 25 mm diameter 2 mm thick LiF disk substrate attached to a rotating stage. The substrate was optically transparent for wavelengths between 180 nm and 600 nm, making it suitable for optical measurements at the maximum of the observed chiral signal at about 530 nm.

Label writing: A label consisting of a predesigned pattern of spots was written by inducing phase transitions in the as-deposited amorphous GST film using 8 ns full width at half maximum pulses with a 10 Hz repetition rate of left- and right-circularly polarized light and linearly polarized light generated using an Nd:YAG laser at a wavelength of 532 nm (second harmonic). In the writing setup, a Glan–Taylor prism was used first as a linear polarizer to prepare 100% plane-polarized light. This light was then incident on a quarter-waveplate with the plane of polarization at a 45° angle with respect to the fast or slow axes of the quarter-waveplate. The laser beam was switched between left- and right-handed circularly polarized states by rotating the quarter-waveplate by 90°. To use the laser beam with linearly polarized light, the quarter-waveplate was removed from the beam path. For writing, the GST film sample was mounted on a movable stage with the film facing the beam and was irradiated by a focused beam of approximately 450 μm diameter with a fluence of 15.5 mJ/cm^2. Spots with three different polarization states, l-CPL, r-CPL and linear-PL, of the incident beam were written in a barcode pattern. The exposure for each spot was 15 s, which produced the largest CD signal for circularly polarized light. The label design and written labels are shown in Figure 1.

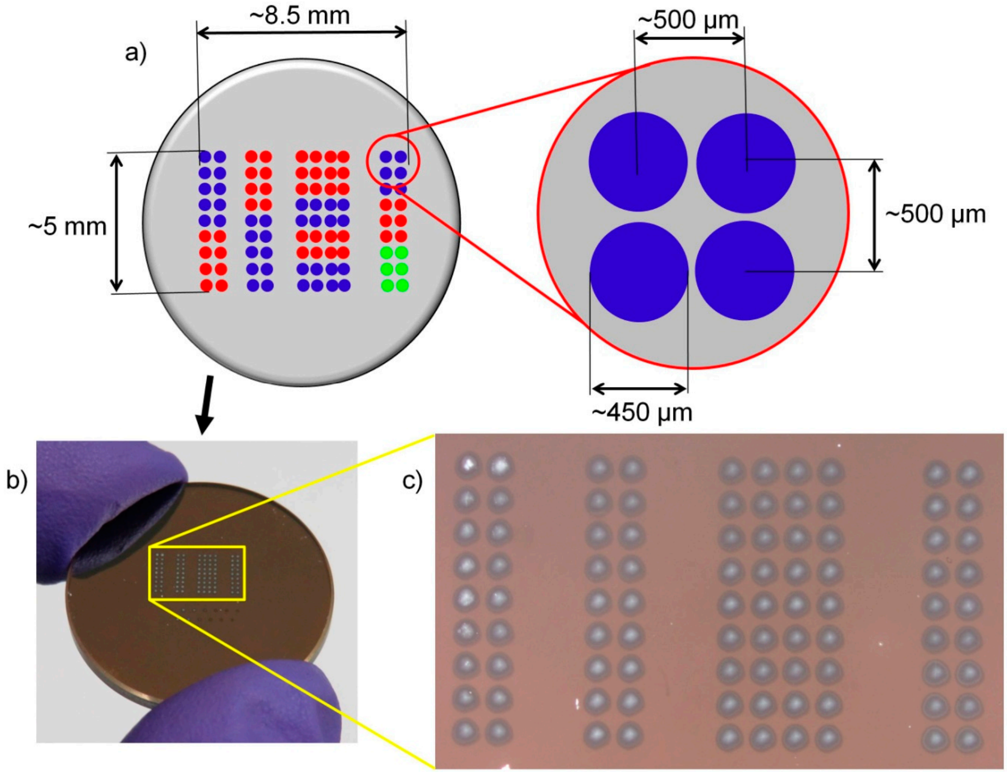

Figure 1. A demonstration label containing covert code within a visible barcode. (**a**) The schematic label design, with the color representing the polarization of the laser beam used to write the spot. Blue—right-circular polarization; red—left-circular polarization; green—linear polarization. (**b**) The label in a sample of GST film on the LiF substrate disk. (**c**) Enlarged barcode observed with unpolarized white light.

Synchrotron circular dichroism (SRCD) spectroscopy and imaging: The individual spots on the sample generated using light of opposite chirality and the original GST film were examined by recording the CD spectra in transmission mode. The spectra were acquired using a collimated and focused synchrotron beam of about 100 μm in diameter in a 200 nm to 600 nm wavelength range with 5 nm intervals. For each spot, scans were recorded with an integration time of 0.5 s for each data point. The resulting spectra are shown in Figure 2.

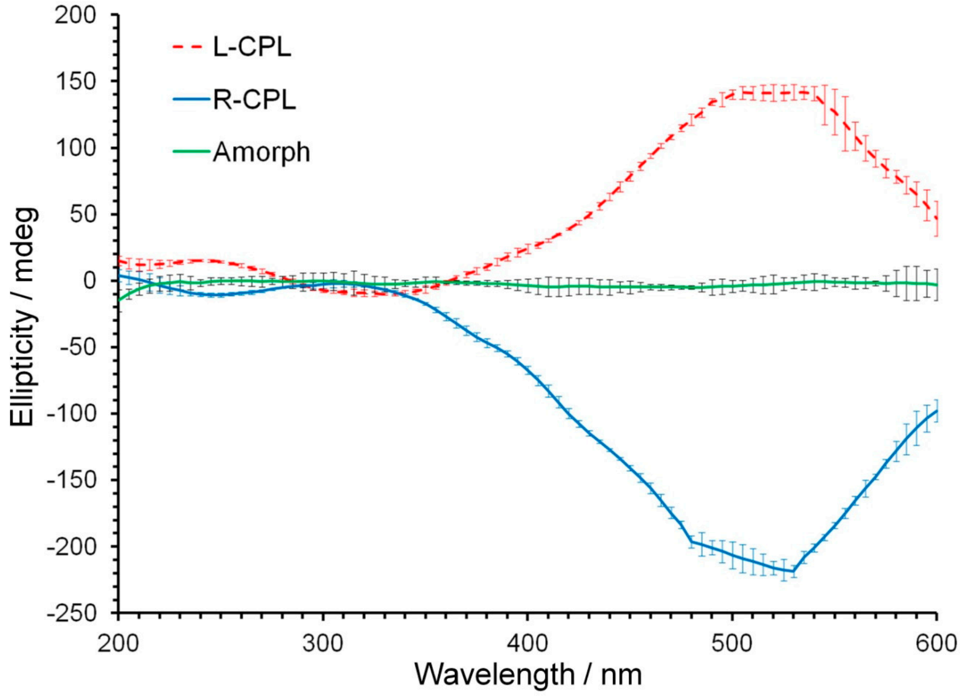

Figure 2. Circular dichroism spectra of spots from a sample label prepared using left- (L-CPL) and right (R-CPL)-circularly polarized light and an as-deposited film (Amorph). The error bars are five times the standard deviations computed from three repeated scans.

To reveal the encoded information, at a single wavelength of 520 nm, at which the CD response has the largest magnitude, an SRCD image was measured in transmission mode from the label area by scanning in a 43 × 26 grid with a 200 µm step [11]. All measurements were performed at the circular dichroism beamline B23 at Diamond Light Source.

Standalone label reader: For the proposed label technology to be practical, reading should not require the use of synchrotron radiation. Here, we demonstrate a standalone label reader, as illustrated in Figure 3.

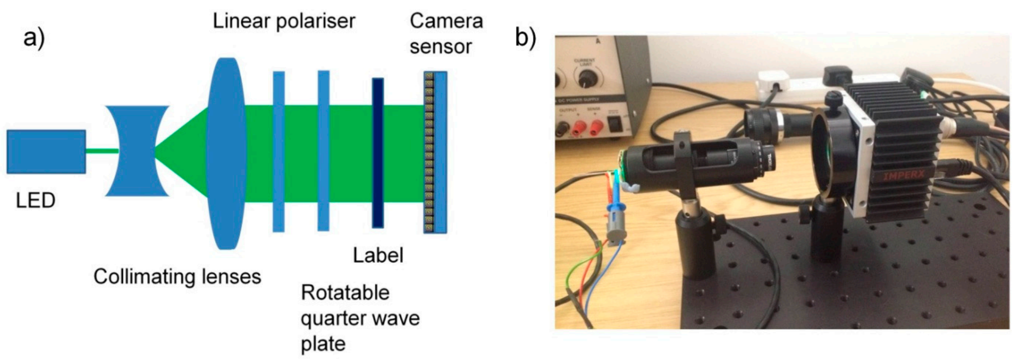

Figure 3. Concept of standalone label reader. (**a**) Schematic of optical design. (**b**) Practical implementation.

The reader consists of a green LED (~520 nm) as a light source, collimating optics to illuminate an area of approximately 1 cm^2, a linear polarizer and a rotatable quarter-waveplate, a sample holder and a camera (12 bit, 1000 × 1000 pixels, 0.49 cm^2 area sensor).

Label reading was performed by illuminating the label with first left- and then right-circularly polarized light by appropriately setting the angle of rotation of the quarter-waveplate and recording the corresponding images. The exposure time was adjusted to avoid saturation of the camera sensor (10 ms), and 256 images for each polarization were recorded. The image intensities were then averaged and converted into ellipticities by applying the formula $\theta \approx \Delta A \cdot 32{,}982$, where θ is the ellipticity in mdeg and ΔA is the difference in absorbance. In the experimental implementation used (Figure 3b), only about a half of the label could be imaged in a single measurement due to the size of the sensor being smaller than the prepared authentication label. The resulting full image of the label was constructed from two consecutive overlapping readings.

3. Results and Discussion

The results of reading the sample label using both SRCD imaging and the standalone reader are presented in Figure 4.

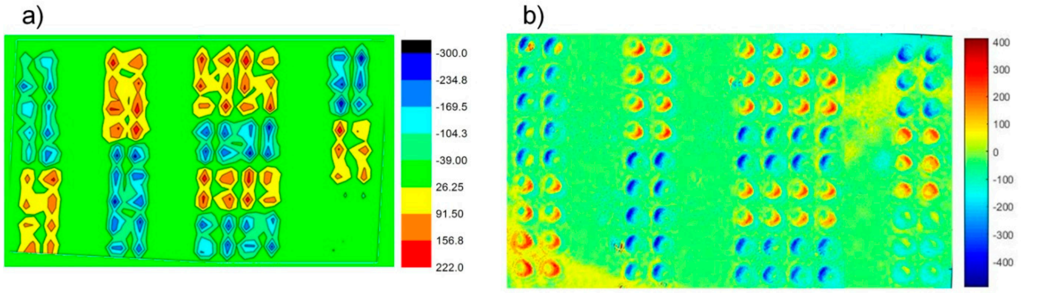

Figure 4. The hidden code revealed by measuring the circular dichroism response of the barcode expressed as ellipticity in mdeg. (**a**) Measured by SRCD imaging. (**b**) Recorded by a standalone reader. Blue—the circular dichroism (CD) response induced by right-circularly polarized light; red—the CD response induced by left-circularly polarized light; green—the CD response induced by linearly polarized light or that of the as-deposited amorphous film.

The light polarization used to write the covert pattern revealed by the standalone reader is in excellent agreement with the results obtained by SRCD imaging.

The results in Figure 4 demonstrate that the polarization state of a writing laser beam can be successfully recorded in the suggested application of an authentication label and read not only by SRCD imaging, but also by a relatively simple standalone device, with excellent qualitative agreement.

Although the direction of the polarization of the spots obtained from the SRCD imaging and the reader agree well, the reader measures an increased range of the ellipticities. This increase in signal may be attributed to considerably higher sampling of the label in the reader (~1,000,000 pixels) compared to the SRCD imaging (~1000 pixels), where it is possible that high-intensity signals are spatially averaged with low-intensity signal areas.

A Gaussian profile of the writing laser beam generates a ring pattern in the spot (Figure 1c), and there are areas within the ring where the CD signal is strongest. According to the results obtained by the reader, the strongest signal is generated by the darker ring of the written spot.

The averaging in SRCD can also explain why the CD spectra of individual spots (Figure 2) display a lower response at 530 nm than that observed by the reader and also the SRCD imaging. The individual SRCD spectra were collected from arbitrarily selected positions within each spot, which, due to the lower resolution of the SRCD spectroscopy, only provide an averaged and, therefore, lower signal.

The observed maximum CD signal is strong, about 400 mdeg, as found by the CD reader, even for a ~450 μm diameter spot. This suggests that a further reduction in size of the written spot is feasible with consequent future miniaturization of this type of authentication label.

The prepared label showed no deterioration in signal when retested after being stored under ambient conditions for at least six months. Preliminary experiments also indicated that the label and the polarization signal remained stable even after short heat treatment at 100 °C, suggesting longer-term stability.

The reading device was tested under ambient conditions. Although a more thorough investigation is required to establish the influence of temperature and humidity on the device, we believe that moderately higher temperatures and lower humidity will not affect the performance of the reading device and the label.

The main challenge in scaling up the proposed technology is expected to be the speed of writing individual labels. We suggest that optimization of the laser power, pulse duration and frequency, number of written areas and automated positioning will be required to manufacture such labels at an industrial scale.

4. Conclusions

We have demonstrated a new technology for writing a covert code invisible to the naked eye. This code can only be revealed if the direction of rotation of the polarization of light encoded in the label during laser writing is measured by a suitable reading device. A prototype of the simple reading device is outlined, which qualitatively provides the same reading outcome as more sophisticated approaches using circular dichroism spectroscopy and imaging. The observed strong signal from the reading device supports further miniaturization of the labels. This feature may enable this approach to be integrated with the technology used in existing holographic security labels to increase the level of security.

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