Personalization of watch components using a novel, switchable PVD coating

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ABSTRACT

Adding a metallic shine, protection, or other decorative features to watch components is often done through physical vapour deposition (PVD) processes. In this paper, we present a novel and extremely versatile type of switchable PVD coating capable of displaying extremely high-quality colours, with near-zero angle dependence on any substrate. More importantly, the coating can be reversibly switched between two or more colours by means of a standard pulsed laser system and without the need for constant energy (batteries, electronics, etc.) to maintain a specific colour state. Colour modulation is achieved by reversibly changing the physical phase of an ultra-thin (<10 nanometre) continuous layer of a Phase Change Material (PCM) sandwiched between two transparent layers. The versatility of this novel non-ink, non-patterning, non-destructive technique is proposed as an entirely new paradigm for the creation and mass-customization of extraordinary watch components.

Keywords: Physical Vapour Deposition, coatings, customization, colour, reversible, laser writing

Introduction

Colouring a watch component traditionally comes with significant limitations in either the breath of colour options, the unwanted presence of angle dependence on the reflected colours or simple difficulty in manufacturing. Furthermore, no alterations can be made to the design after manufacturing, without disassembling the entire watch and removing the dial for a replacement. In this paper, we present a highly versatile type of PVD coating that can not only be used to add any colour to a watch dial, or virtually any other surface, but that furthermore can have multi-coloured decorations added at any point in manufacturing, or even after the sale of the watch. To enable such a technology, we have drawn inspiration from nature. Animals and plants display colours for a variety of purposes including mating, attracting preys, and avoiding predators. Although most colours in nature are a result of pigmentation, or the light absorption characteristic of specific compounds, there are several examples of organisms that use complex light interference techniques to filter ambient light into incredibly intense and pure colours. Common examples are the beautiful blue wings of the morpho butterfly or the strikingly white reflective scales of the cyphochilus beetle. Interestingly, these animals do not truly “posses” these unusual colours; they are the result of light interfering with peculiar nanoscale-sized structures present on their bodies. Altering these special structures, by destroying them or covering them with a transparent liquid for example, will neutralise the interference effect revealing their intrinsic and very much unremarkable pigmentation. Our novel PVD technology uses the tuneable optical properties of a particular class of solid-state, inorganic chalcogenide materials know as Phase Change Materials (PCM) to create unique and vibrant colours entirely by light interference [1]. PCM are well-known functional materials with a long history of commercialization in data storage technologies such as re-writeable optical discs (DVD-RW, Blu-Ray) [2].

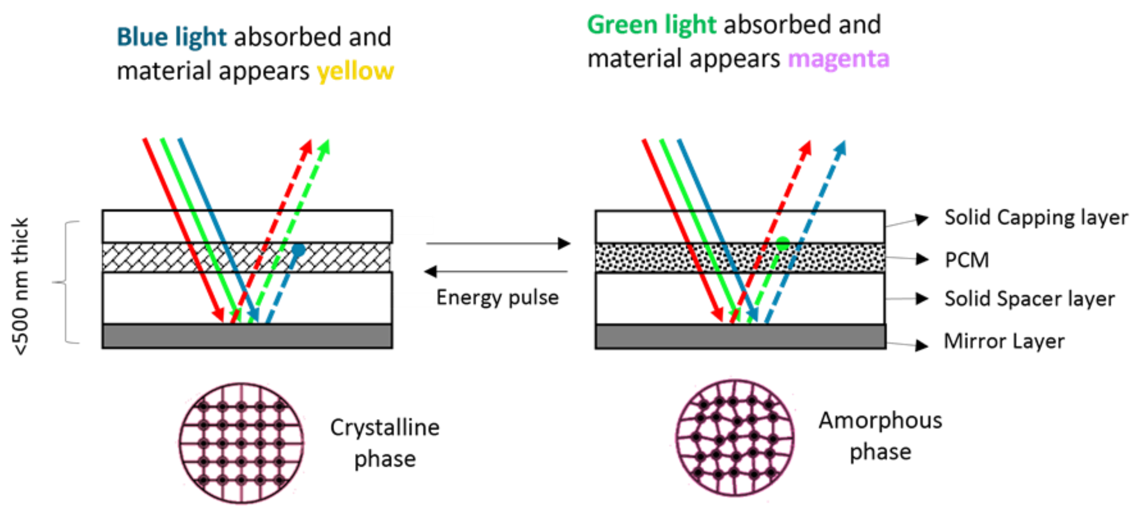

Figure 1 – The fundamental structure of the switchable, PCM-based colour technology. The multi-layered stack includes a mirror layer, a solid spacer layer, a PCM layer and a top capping layer, deposited in sequence without breaking vacuum, with a standard PVD sputtering system. The colour reflected off the surface can be tailored precisely by designing and choosing the thickness of each layer during deposition. The PCM layer can actively and precisely change the interference condition (i.e. colour) of the cavity depending on which state they are set at the time.

Results and discussion

The basic structure of the PVD coating is shown in **Figure 1**. The multi-layered stack includes a mirror layer, a solid spacer layer, a PCM layer and a top capping layer, deposited in sequence with a standard PVD sputtering system. The colour reflected off the surface can be precisely tailored by choosing the thickness of each material during deposition. The simple three-layered stack of **Figure 1** can display an extremely large variety of saturated and bright colours.

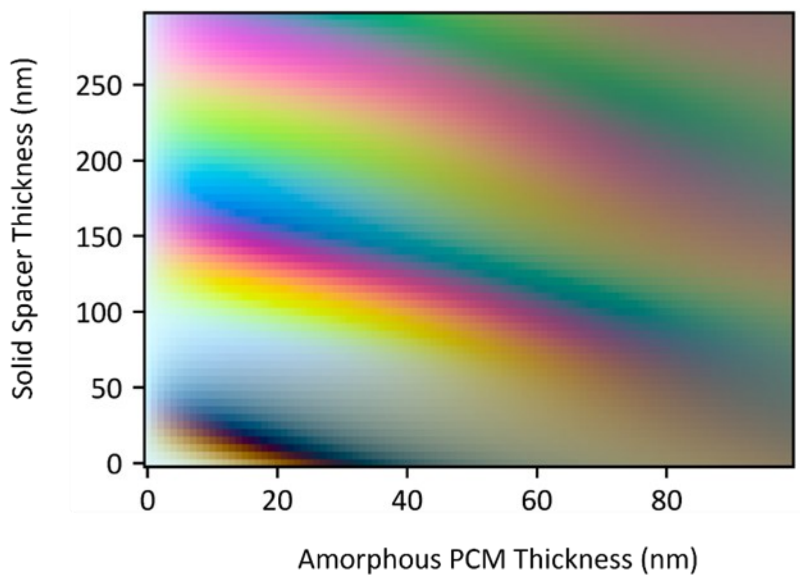

Figure 2 – Dependence of the physical thickness of the PCM (amorphous phase) and solid spacer to the overall reflected colour of the stack. The colours are calculated using a robust thin-film transfer-matrix approach.

Figure 2 shows a collection of simulated colours for this stack, calculated using a robust thin-film transfer-matrix approach, by changing the thicknesses of the solid spacer and PCM layers with steps of 1 nm. Importantly, the most vibrant colours, as well as simple black and white options, are obtained for films with PCM thickness around 10 nm and spacer thickness below 250 nm. Interestingly, this ultra-thin nature of the coating gives it a remarkable low angle dependence with respect to colours, as well as an inherent mechanical flexibility.

The ability to show beautiful colours and special effects, on any substrate, using standard PVD thin-film techniques are only a small part of the capabilities that the PCM technology offers to the watchmaker. As mentioned previously, PCM are functional materials with tuneable optical properties originally formulated to serve the optical disc data storage industry. They are inorganic materials capable of switching between at least two stable states known as the amorphous phase and crystalline phase. These states have very different optical characteristics with the amorphous phase having semi-insulating and semi-transparent properties and the crystalline phase having semi-metallic and reflective characteristics. When integrated into an optical cavity, like the stack shown in **Figure 1**, the PCM can actively and precisely change the interference condition (i.e. colour) of the cavity depending on which state they are in. For example, a stack can be designed to show a precise shade of yellow colour when the PCM is in the amorphous phase and a magenta colour when the PCM is in the crystalline phase. Importantly, the PCM can be reversibly switched between its phases up to millions of times without changes to the optical performance; data storage applications use this re-writability feature to record data as "0" and "1" on DVD-RW and Blu-Rays discs. **Figure 3** shows a variety of colour swatches deposited using the same materials with different stack designs. Each colour pair is shown for both the amorphous and crystalline phases. The same collection of samples is photographed at two different angles to demonstrate the very low angle dependence of the colours.

Figure 3 – Various colours obtained by tuning the thickness of the PCM based, thin-film stack. Each stack is shown in both the amorphous and crystalline phase. The same collection of stacks is photographed at two different angles to demonstrated the low angle dependence obtainable by the technology.

A brief explanation of PCM switching mechanism is given in **Figure 4a**. PCM materials have two, well defined, transition temperatures that play a fundamental role in the switching mechanism: a crystallization temperature (Tc) and a melting temperature (Tm). Starting from amorphous PCM thin-films, these are commonly deposited using standard, room-temperature PVD sputtering techniques. Increasing the temperature of an amorphous film to above Tc crystallises the ultra-thin PCM layer in less than a microsecond. Once crystallised, the overall stack has permanently changed colour and no additional energy is required to maintain the new state. To switch the material back to the initial amorphous phase, the temperature of the layer must now increase above Tm (melting point of the PCM layer) and cooled quickly enough so that the PCM layer does not have time to re-crystallise, quenching back the layer to the initial amorphous phase. The melt-quenching process is entirely passive (i.e. the PCM layer does not need to be actively cooled) by using the continuous mirror as the heat dissipating medium. In practice, nanosecond-long heat treatments can only be achieved by means of laser excitation or electrical excitation. Laser excitation in particular offers great benefit in terms of local and precise personalization of the coating and, in the case of PCM technology, numerous chances of personalization and modifications over the lifetime of the product. **Figure 4b** demonstrates an example of laser "writing" of a PCM-based optical stack. The coating was deposited on a standard 2-inch glass wafer (borofloat33) and was designed to switch from an initial gold colour (amorphous phase) to a dark purple colour (crystalline phase) upon laser excitation. An XY laser scanning system equipped with a 5W, 405 nm, blue laser diode and controlled via a dedicated software was used to switch between the two states of the coating. The resolution of the technology is theoretically infinite; however, in practice the resolution depends on the size of the laser spot used to locally crystallise the stack. An example of an image written with a higher resolution system is demonstrated in **Figure 4c** where each dot written measures roughly 5 µm in diameter. Dots as small as 50 nm have been switched previously using a Conductive Atomic Force Microscope (CAFM) as a conclusive demonstration of the ultra-high, beyond-printing resolution achievable with the technology [1].

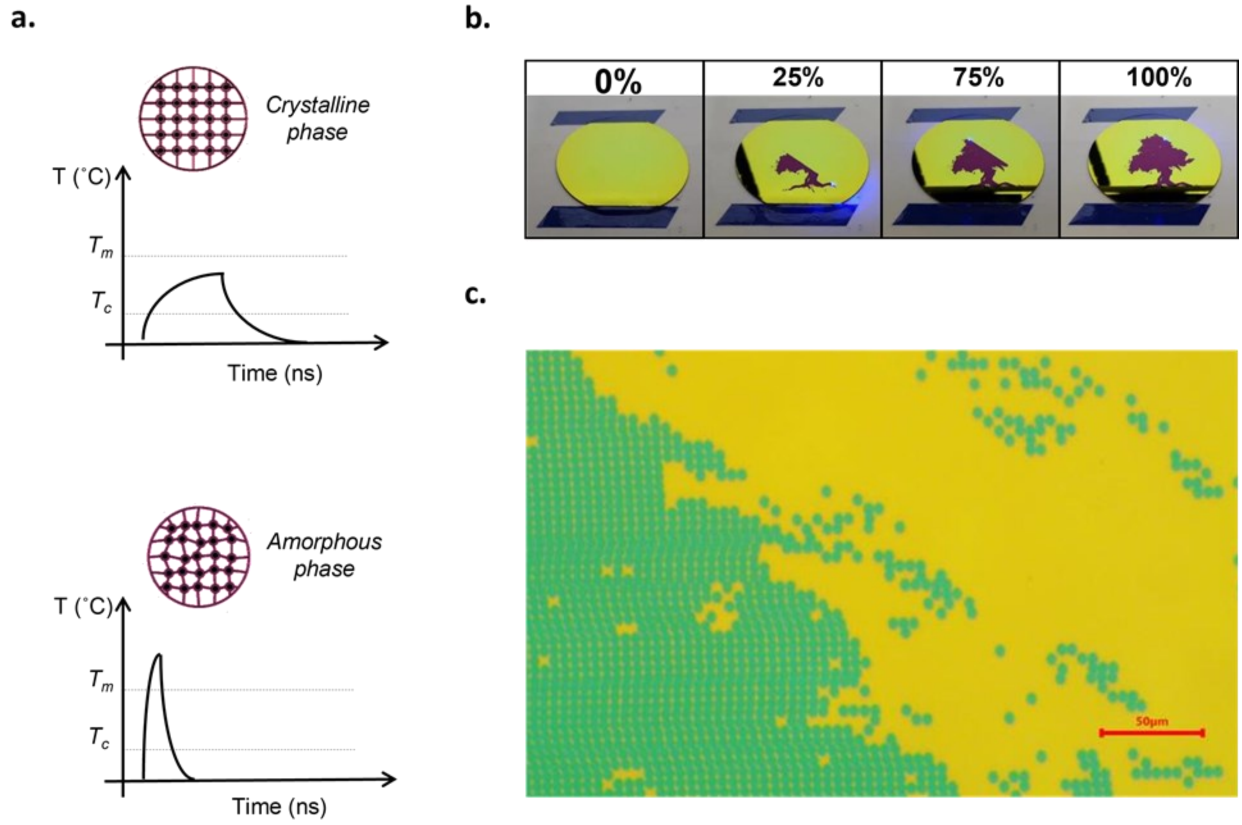

Figure 4 – a. Switching mechanism of PCM thin films. Increasing the temperature of an amorphous film to above Tc will crystallize the PCM layer in less than a microsecond. To switch the material back to the amorphous phase, the temperature of the layer must now increase above Tm (melting point of the PCM layer) and cooled quickly enough, quenching back the layer into this phase. b. An example of laser "writing" of a PCM-based optical stack. c. An example of an image written with a higher resolution system. Each dot measures roughly 5 µm in diameter.

From a thermodynamics point of view, the amorphous phase is a metastable state that will ultimately crystallise, if given an infinite amount of time to do so. However, from a user perspective and for temperatures below 100°C, crystallization will naturally occur only after several decades. Once it is crystallised, the material can always be reset back to its amorphous phase using the same crystalline to amorphous melt-quenching treatment described earlier. The amorphous-to-crystalline-to-amorphous switching process can be run millions of times without changes to the optical performance of the stack.

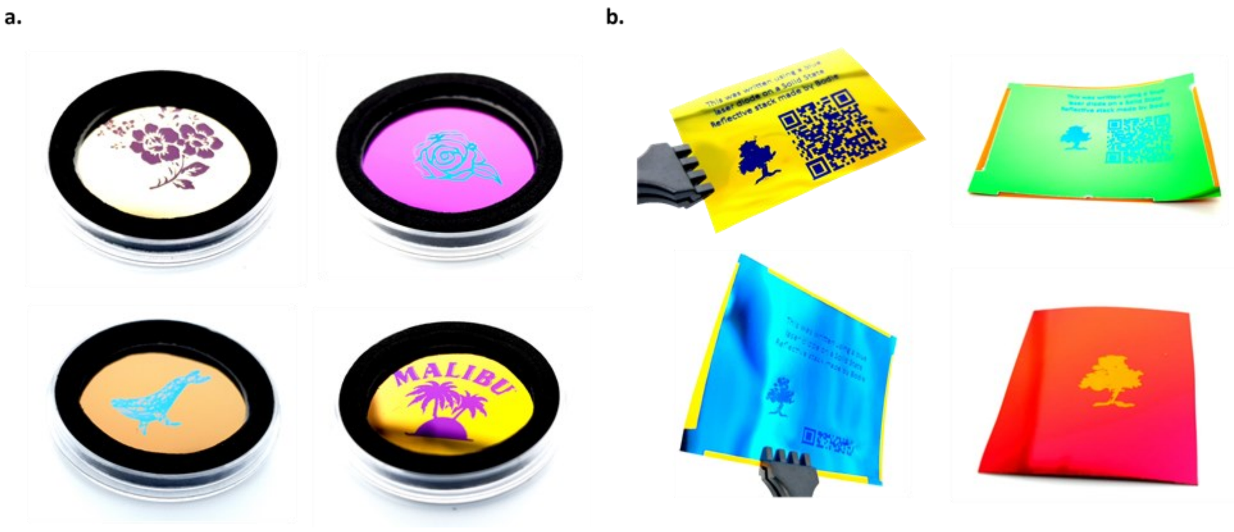

Figure 5 – Several examples of laser written PCM based stacks on both a. rigid substrates and b. flexible substrates. The samples were written using a pulsed blue laser diode system controlled via a dedicated software.

Years of development, better materials and more advanced stacks have further amplified the design flexibility of the PCM based technology [3]. Examples include the ability to display highly saturated primary colours with low angle dependence as well as goniochromatic effects on any substrate and without the need for any surface modification or patterning. Finally, iridescence can be also added as an option on one, both or none of the PCM states, depending on the design requirements. A collection of further examples is shown in **Figure 5** for both rigid (**a**) and flexible (**b**) substrates. It is important to highlight that all colours were deposited using the same PVD system, the same materials and by only changing the design (i.e. thicknesses) of the stack. Crystallization was achieved using a single blue laser diode for all colours and substrates.

Application to watchmaking

PCM-based thin-films have the potential to create an entirely new paradigm of smart decorative coatings available to the watch designer. The possibility of coating a multitude of materials and components such as dials, hands, markers, etc. together with the unique capability of laser driven colour switching could enable a new generation of mass-customisable products both in-factory and in-store. Remarkably, the uniform nature of the PCM coatings allows integration with surface patterning techniques that already create retro-reflective, prismatic or diffused finishes to materials and components. **Figure 6** shows a few examples of PCM stacks deposited on watch dials with common types of surface finish. Where the dial was made with a soleil pattern, the pattern and corresponding optical effect remains even after the application of the ultra-thin PCM coating (**Figure 6a**). Similarly, a dial with a perfect mirror finish will retain the specular nature of the light reflected off its surface even after the application of the PCM coating (**Figure 6b)**. More importantly, **Figure 6b** demonstrates how the PCM coating (in this case a gold to cyan stack) can be written directly with a laser without affecting the quality of the reflection. Unwated effects such as diffusive damage, haziness, milkyness, bleaching do not appear even after time. The ultra-thin, ultra-light, non-altering nature of the coating further adds to the ease of integration with existing functional and mechanical components. Finally, the technology might be of particular interest to the traditional watching making industry thanks to the ability to retain the custom patterns without any need for batteries or electronics of any kind.

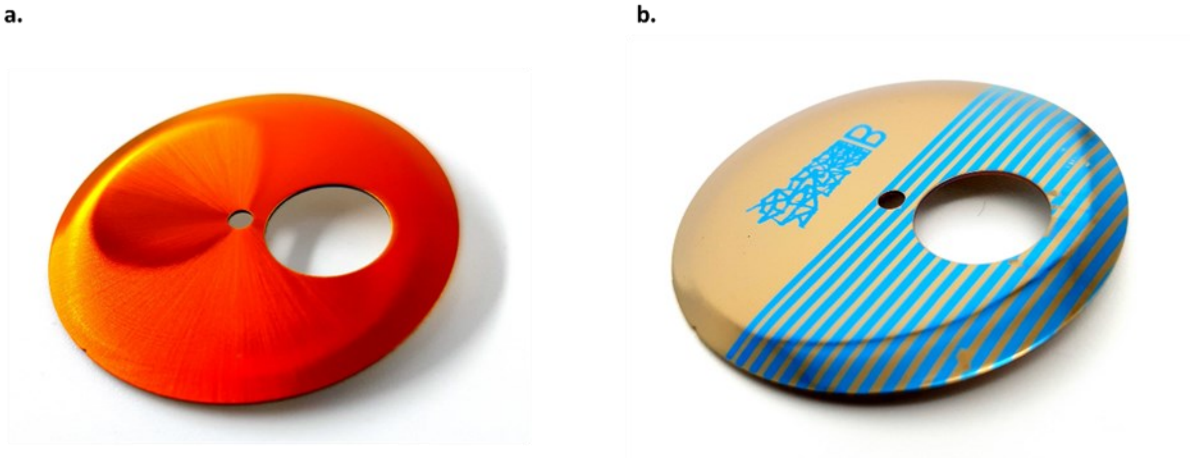

Figure 6 – Examples of PCM film deposited directly on two different types of watch dials. **a.** Dial with a soleil pattern; the pattern and corresponding optical effect remain after the application of the ultra-thin PCM coating. **b.** Dial with mirror finish coated with a gold to cyan PCM stack; the quality of the light reflection remains after PCM deposition. A laser was used to write a predefined pattern directly on the dial after PCM deposition. Laser switching does not introduce unwanted optical effects such as diffusive damage, haziness, milkyness, bleaching.

References

1. Hosseini, P., C.D. Wright, and H. Bhaskaran, *An optoelectronic framework enabled by low-dimensional phase-change films.* Nature, 2014. **511**(7508): p. 206.

2. Wuttig, M. and N. Yamada, *Phase-change materials for rewriteable data storage.* Nature Materials, 2007. **6**: p. 824.

3. Talagrand, C., et al., *Solid-state reflective displays (SRD®) for video-rate, full color, outdoor readable displays.* Journal of the Society for Information Display, 2018. **26**(10): p. 619-624.