PHASE-CHANGE MATERIALS

Designing optical media of the future

Over the past two decades, the optical recording industry has empirically improved the properties of phase-change materials for rewritable discs. Now a first step has been taken to use computational design to improve these materials.

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Chalcogenide phase-change materials are the key components used for rewritable optical discs, and improving the speed of imprinting information is of significant commercial interest. Much effort is therefore being expended in the development of these materials, but prediction of the various relevant and desired properties to increase possible writing speeds is difficult, as they are intimately related to the structural changes at the atomic scale. On page 122 of this issue, Matthias Wuttig et al.1 take a big step towards the ability to design novel phase-change materials. By using ab initio density functional theory and an improved understanding of the mechanisms behind the structural phase change2,3, the authors are able to predict the stability of the crystalline state. This could provide valuable information for determining the suitability of chalcogenide materials (for example, Ge–Sb–Te) not only for future optical recording media but also for phase-change random access memories4 (PCRAM).

Optical writing and erasing bits on a disc is done by heating small spots of a phase-change layer with a focused laser beam, as shown in Fig. 1. Writing involves first the melting of the phase-change material at around 600 °C, followed by a very short cooling time of a few nanoseconds. This enables the material to solidify into an amorphous state, which constitutes the physical representation of a written bit. As the crystalline and amorphous state of the phase-change material have different optical properties, the difference between a crystalline or amorphous spot (or bit) can be read by measuring its reflectance. For erasing a written bit, the same spot of the phase-change layer is heated to only a few hundred degrees Celsius, but now for a duration of tens of nanoseconds. This enables the amorphous material to return into the crystalline state.

Since the first observation of reversible laser-induced amorphous–crystalline transitions by Ovshinsky et al.5,6,7,8,9, optical recording industry has been pushing to shorten the bit erase time, because it is the limiting factor for achieving larger recording speeds. Nowadays a commercial DVD recorder can write a DVD eight times faster than its normal playback speed, corresponding to bit rates as high as 100 Mbit s−1 and erase times of a few tens of nanoseconds. Two classes of phase-change materials were discovered that could deliver these short erase times, enabled by their fast crystallization speeds6: nucleation dominated materials (NDM), first introduced by Matsushita/Panasonic and fast-growth materials8 (FGM), first introduced by Ricoh. The NDM family has Ge,Sb,Te (GST 225), Ge,Sb,Te and Ge,Sb,Te as its thermodynamic stable ternary compositions6, all residing along the pseudobinary GeTe–Sb,Te tie-line, as

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interstitial fluid, the effective load experienced by the contacting collagen matrices is much reduced and the friction between them is eased.

In this context, the paper by Moutos and co-workers provides a breakthrough in the design of scaffolds whose initial mechanical properties match those of native articular cartilage7. These authors have developed a microscale three-dimensional weaving technique to produce scaffolds from yarns made of a biocompatible material such as polyglycolic acid. The fibres in this scaffold are oriented in three orthogonal directions, so as to produce a material with different properties along each of its planes of symmetry. The resulting scaffolds are porous, and the authors filled them with a cell-seeded hydrogel such as agarose or fibrin in which the round morphology and cellular functions typical of chondrocytes can be maintained.

Most remarkably, these constructs not only mimic the fibre-composite structure of the native cartilage but they also reproduce the disparity observed between the tensile and compressive stiffness of the tissue, which are critical to load bearing and lubrication. Because the initial mechanical properties of these scaffolds are quite similar to those of native cartilage, it is likely that these constructs will survive the harsh loading environment of the joints immediately after implantation.

This approach represents a paradigm shift in the field of cartilage tissue engineering, which heretofore had proposed that constructs would slowly acquire normal mechanical properties following implantation. The availability of biocompatible, slowly degrading constructs whose initial mechanical properties can be tuned over a broad range (owing to the versatile manufacturing technique) that encompasses those of native cartilage makes it possible to test the hypothesis that initial construct stiffness is critical to the long-term survival of implanted artificial cartilage. The basic premise of this approach is that chondrocytes need to be shielded from excessive compressive strains over a sufficiently long period of time, typically exceeding normal postoperative recovery periods, while they slowly synthesize the collagen matrix critical for their normal function. So the scaffold made by Moutos and co-workers represents a major advance towards this goal, providing an exciting opportunity for cartilage tissue engineers.
shown in Fig. 2. The FGM family is based on the binary composition Sb$_2$Te$_3$.

Although the erasure time of bits at elevated temperatures is very short, the archival lifetime of an amorphous written bit must still be long enough at room temperature so as not to lose the information stored by the user. Therefore, at user conditions extremely slow crystallization is required. The crystallization speed at elevated and moderate temperatures is empirically connected to the stability of phase-change materials, which is quantitatively expressed by the energy that is needed to form a particular compound.

It is this energy of the cubic (metastable) crystalline phase, the phase after bit erasure, that has been calculated by Wuttig et al. using ab initio density functional theory. Their calculations for a series of materials closely related to the NDM family in the Ge–Sb–Te ternary system, see Fig. 2, have led the authors to the prediction of more stable cubic crystalline phase-change materials. These new compositions do not reside on the pseudobinary GeTe–Sb$_2$Te$_3$ tie-line, where the thermodynamic stable compositions with a hexagonal phase can be found.

Starting with the energy calculations of the cubic Ge$_2$Sb$_2$Te$_5$ compound, the authors show that a more stable composition can be obtained by taking away Ge atoms, thus creating vacancies. The energy is found to be minimal at about 12% of vacancies, when ‘walking’ the red dotted line in Fig. 2 from Ge$_2$Sb$_2$Te$_5$ to Ge$_2$Sb$_2$Te$_7$. A vacancy concentration of 12% corresponds to the composition Ge$_{18}$Sb$_{34}$Te$_{78}$. The authors observe a similar phenomenon when ‘walking’ the blue dotted line from Ge$_2$Sb$_2$Te$_5$ to Ge$_2$Sb$_2$Te$_7$, yielding a minimal energy for the composition Ge$_{20}$Sb$_{31}$Te$_{79}$. The occurrence of a minimum in energy of the cubic (metastable) crystalline phase along the red and blue dotted lines is intriguing. One would expect a monotonous decrease in energy on the removal of Ge atoms, as it is commonly believed that Ge–Te forms the strongest bond in the Ge–Sb–Te ternary system.

Based on their results, Wuttig et al. attribute the observation of a minimum to the formation of antibonding Ge–Te interactions that occur when the number of Ge atoms becomes too large. These findings represent an important step in the ongoing efforts to improve phase-change material properties, as it is shown for the first time that an important property, such as the energy required to form a compound, can be predicted in advance. Such predictions will also be relevant for the emerging field of PCRAM. Whatever the applications, the work by Matthias Wuttig and co-workers provides us with the capability to design the appropriate phase-change material.

References