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New process for optical information storage

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We propose a new process for optical information storage, which allows low-power writing while ensuring high stability. We demonstrate experimentally the operation of this mechanism in iridium oxide films.

Much current research is devoted to investigating new materials and processes for mass storage of information.[1] An example is the search for more efficient optical disk-storage media. Although the optical disk technology appears to be very promising, there are two major problems impeding its development.[2] Namely, the writing process should require low power and the writing medium should be highly stable (e.g., >10-yr archival time). These two requirements appear *a priori* mutually exclusive. In fact, low power implies a low thermodynamic barrier for the writing process, whereas high stability requires a high thermodynamic barrier for the "erasing." Thus materials in current development sacrifice one property to the other. Indeed, the process of choice is melting, which can ensure stability, but at the expense of a very high writing power.

In this Communication we propose a new mechanism of optical information storage, which allows low-power writing while ensuring high stability. We demonstrate experimentally the operation of this mechanism in iridium oxide films.[3,4]

The fundamental idea of the mechanism is based on producing a thin-film material in a thermodynamically metastable state, optically distinct from its stable state. The stable state must be accessible directly from the metastable state (i.e., we are excluding processes wherein the stable state is accessible only through an intermediate third phase). In this case, writing via the transition from the metastable state M to the stable state S (see Fig. 1) can take place at low energy, whereas erasing can only take place by surmounting the high-energy barrier for the reverse (S to M) transition.

The metastable state must be sufficiently stable at ambient temperatures to allow long-term archival storage, which precludes materials with short-lived transient metastable states. M to S transitions are of two kinds. Either M and S are compositionally identical or they are not. Examples of the first kind are amorphous to crystalline transitions (not via melting). Examples of the second kind are decompositions, dehydrations, etc. Both kinds of M to S transitions could be used for writing, but the latter mechanism may be preferable if reversibility is desired. In some applications it is advantageous to be able to reverse the writing process and erase the written information. This, in principle, can be done in those cases of M to S transition where the stable state is achieved by a topotactic[5] extraction of a component. Reinsertion of the same component restores the original state. An example of this kind of M to S process is provided by dehydration-hydration effects, i.e., rehydration may be effected by a different process to that which caused dehydration.

To demonstrate both kinds of M to S transitions and show the potential of dehydration-hydration effects for applications, we have investigated reactively sputtered iridium oxide films (SIROF's).[3,4] These films have unusual electrocatalytic[6] and electrochromic[3,4] properties. Their most remarkable characteristic is their high stability (essential for information storage) and absence of corrosion in a wide variety of electrolytes.[7] SIROF's are hydrated oxides of iridium but the ratio of components (Ir, O_2, and H_2O) can

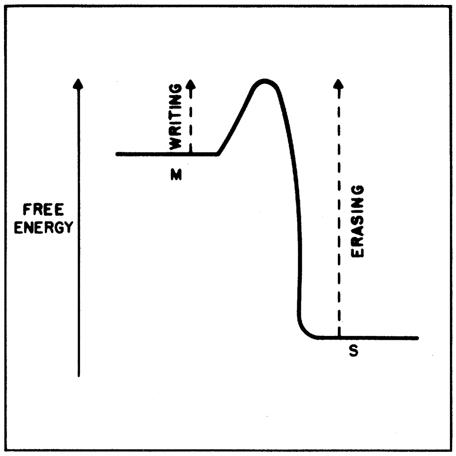

FIG. 1. Schematic free-energy diagram for a material with a thermodynamically metastable state (M), optically distinct from its stable state (S). The latter must be accessible directly from the metastable state (i.e., we are excluding processes wherein the stable state is accessible only through an intermediate third phase). In our case the main M to S process is produced by dehydration.

vary with the preparation. On the other hand, their stoichiometry and structure are critical to the extent that compositionally very similar films do not exhibit the same properties.[8,9] For example, crystalline IrO_2, with a rutile structure, is not electrochromic.[10] Anodically grown films are electrochromic but have poor stability.[9] Similarly, "blue" SIROF's[10] are not highly stable.

We have recently investigated[8,11-13] the SIROF's structure and composition by differential thermal analysis, evolved gas analysis, scanning electron microscopy (SEM), x-ray diffraction, and electrical conductivity. Three events were identified: (1) water loss occurs at ~100 °C; (2) a structural transition from amorphous to crystalline rutile occurs at ~300 °C; and (3) a decomposition with dehydration takes place at ~700 °C. The first two events are of interest to us here since they are clear examples of the two kinds of M to S transitions discussed above.

In Fig. 2 (dashed-dot curve) the resistivity ρ as a function of temperature is reproduced from Ref. 8. The two M to S transitions are clearly identified. The decrease in ρ starting at ~100 °C corresponds to the dehydration transition. The decrease starting at ~300 °C corresponds to the amorphous to crystalline transition.

Corresponding to these transitions, we have investigated these films for optical changes since dehydration[14] of mixed valence materials may lead to color changes. Sputtered iridium oxide films were prepared on SiO_2 substrates as described in Refs. 15 and 16. The films were deposited by reactive rf sputtering in a commercial, conventional diode sputtering system in 80:20% mixture of argon and oxygen at a target bias of 1 kV and forward power of 100 W. Films of different thicknesses were prepared, from 1000 to 5000 Å. The samples were heated in a tube furnace with quartz windows at either end so that optical changes could be recorded. The rate of heating of the furnace was ~50 °C per minute. This fast rate of heating probably allows the temperature of the substrate to be somewhat lower than the furnace temperature due to its thermal mass, as was indicated in the resistivity measurements.[8]

Reflectivity and transmission were measured at 633 nm using a He-Ne laser and a silicon photodiode detector. Figure 2 shows the transmission (dashed line) and reflectivity (solid line) as a function of temperature for a SIROF ~4000 Å thick. It is clear that the two transitions previously established are also observed in the optical changes. Indeed, significant changes accompany the dehydration transition as well as (albeit less markedly) the amorphous to crystalline transition. The rise in transmission at high temperature corresponds to the decomposition of the film. More insight into the details can be gained by laser writing, as illustrated in Fig. 3.

Figure 3(a) shows the optical transmission micrograph of a line written by an argon laser at 0.8-W total power. Laser writing produces six optically different regions [schematically represented in Fig. 3(b)] and modifies the sample profile as shown in Fig. 3(c). The appearance of the six regions can be easily understood in the light of thermal annealing data (Fig. 2). Since the laser beam power peaks along region 6, the sample temperature decreases

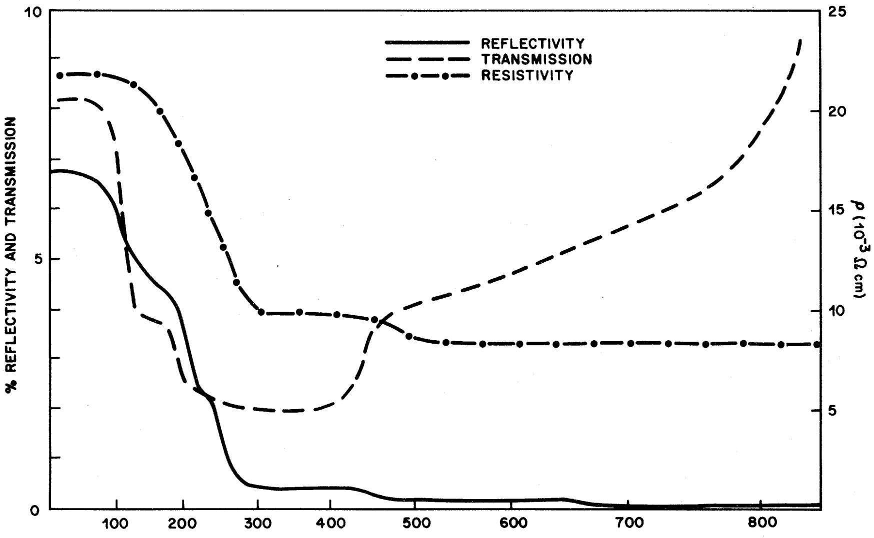

FIG. 2. Resistivity (dot-dashed line), transmission (dashed line), and reflectivity (solid line) as a function of temperature for SIROF's ~4000 Å thick. The two M-to-S transitions are identified at ~100 and 300 °C, corresponding to dehydration and crystallization, respectively.

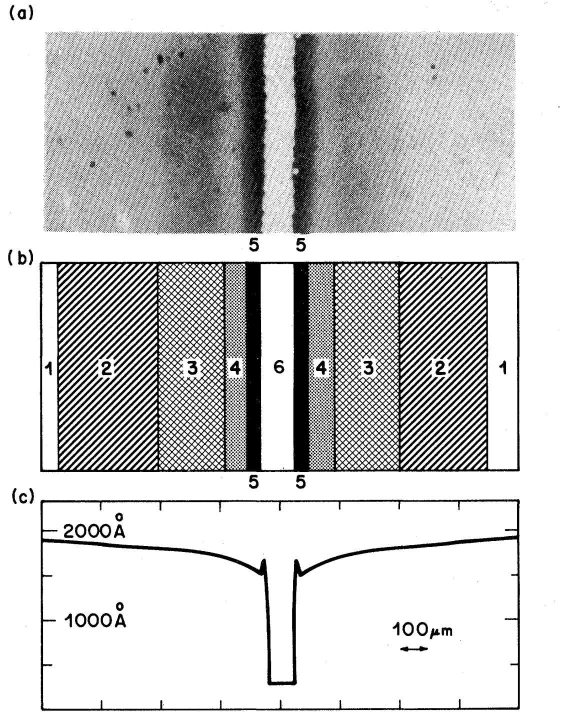

FIG. 3. (a) Transmission optical micrograph of a line written with cw argon laser at 0.75-W total power. (b) Schematics of the six optically distinct regions. (c) Profile of the film.

from region 6 to region 1. From 1 to 2 and from 2 to 3, the SIROF undergoes dehydrations resulting in a darker appearance (two dehydration transitions are visible in Fig. 2—transmission—at ~150 and 200 °C). From 3 to 4, the sample undergoes the metal-insulator transition [the lighter appearance in Fig. 3(a) corresponds to the increased transmission at ~420 °C in Fig. 2]. The last two regions (5 and 6) are not due to metastable to stable transitions but are the product of morphological changes. The high laser power carves a "groove" in region 6 and thus produces a "ridge" in region 5. SEM data show that the sample is smooth (on the 100-Å scale) from regions 1 to 4, whereas it exhibits roughness on the scale of >1 μm in region 6. The dark appearance of region 5 is due to the presence of roughness on the scale of optical wavelengths. More detailed experiments on laser writing of iridium oxide films are being carried out in this laboratory.[17,18]

In conclusion, we have proposed a new mechanism for information storage suitable for optical writing. We have demonstrated experimentally that this mechanism allows writing with low power on a highly stable medium.

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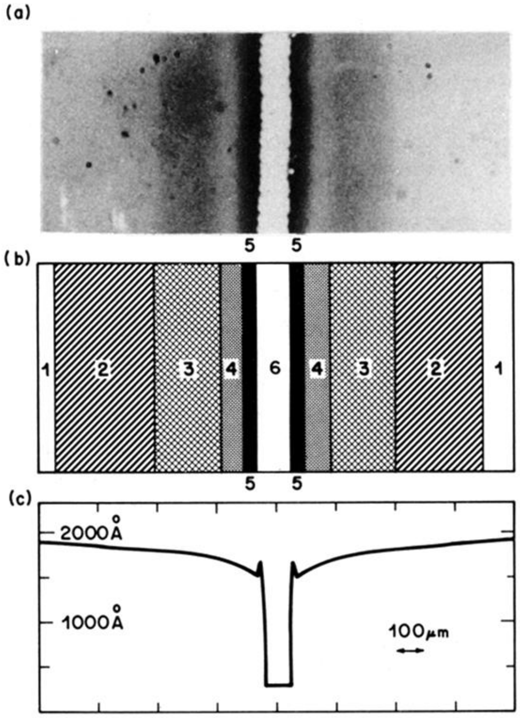

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