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COMMUTON – A NEW CONCEPT IN SWITCHING MATERIALS

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A switching unit can be defined as the smallest unit that preserves the property of switching in memory materials. Atomic switching unit is discussed, molecular switching units are described and supramolecular units in phase change materials are evidenced and discussed. The "commuton", as basic switching unit, could give more insight into the particular properties of the switching phenomena in various solid materials.

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1. Introduction

The switching in materials is the most interesting phenomenon discovered in materials, both organic and inorganic. The switching materials opened a large class of applications in electronics and informatics. The use of switching in computer memories, in information recording (CD or DVD), and the applications in automation and robotics are well known. Phase change materials are the leading class of solids were the transition amorphous-crystal and back is controlled for getting a switch usable in computer memory. The switching effect was discovered by Ovshinsky [1] in the $Te_{40}As_{30}Si_{12}Ge_{10}$ amorphous chalcogenide.

In this paper we try to show that in switching materials is possible to define a minimum switching unit that ensures the change of state. This switch unit has been called: commuton.

2. The atomic level switch (atomic *commuton*)

In electronics, a switch is an electrical component which can break an electrical circuit, interrupting the current or diverting it from one conductor to another [2]. The most familiar form of switch is a manually operated electromechanical device with one or more sets of electrical contacts. Each set of contacts can be in one of two states: either 'closed' meaning the contacts are touching and electricity can flow between them, or 'open', meaning the contacts are separated and non-conducting. The smallest switch unit is the atomic switch. In the atomic switch the existence of minimum two states is essentials. These states could be quantum states or states of different electron distribution. The atom can be triggered from the un-excited state to an excited state and back. Another property of the atom useful in switching devices or spintronics is the spin. Different orientations of the spin of one atom can be triggered according to an excitation quantum.

3. The molecular switch (molecular *commuton*)

Rotaxane-based molecular machines have been of interest for their potential use in molecular electronics as logic molecular switching elements and as molecular shuttles [3, 4]. The chemical structure of rotaxane is shown in Fig. 1. The molecular machines are based, for example, on the movement of a macrocycle on the dumbbell. The macrocycle can rotate around the axis of the dumbbell like a wheel and axle or it can slide along its axis from one site to another. By controlling the position of the macrocycle allows the rotaxane to function as molecular switch with each possible location of the macrocycle corresponding to a different state (Fig. 2). These rotaxane machines can be manipulated both by chemical [5] and photochemical inputs [6]. Rotaxane based systems have also been demonstrated as molecular muscles [7].

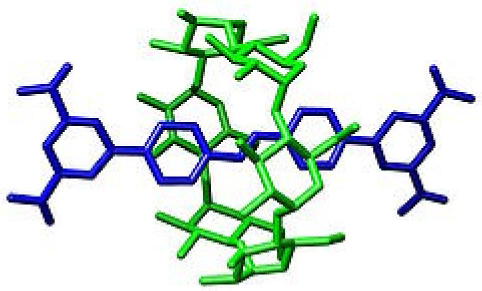


Fig. 1. Crystal structure of a rotaxane with an α-cyclodextrin macrocycle [7].

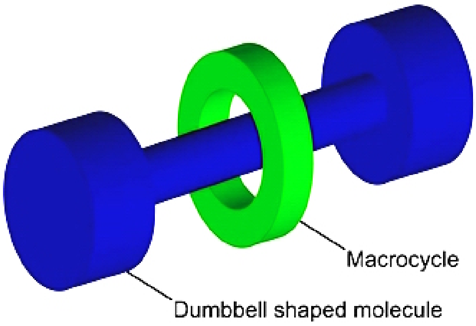


Fig. 2 Schematic of the rotaxane molecule

In a nano-recording application [7] a certain rotaxane is deposited as a Langmuir-Blodgett film on ITO coated glass. When a positive voltage is applied with the tip of a scanning tunneling microscope probe, the rotaxane rings in the tip area switch to a different part of the dumbbell and the resulting new conformation makes the molecules stick out from the surface by 0.3 nanometer and this height difference turns out to be sufficient for a memory dot. The 160-kilobit memory device using interlocked molecules is the result of the research of a team at the UCLA laboratory of J. Fraser Stoddart, director of the California NanoSystems Institute (CNSI). The memory employs a series of perpendicular, crossing nanowires, 400 above and 400 bellow. At each crossing are found about 300 bistable rotaxane molecules, serving as the storage element, and can be switched between two different states, and each junction of a crossbar can be addressed individually by tuning the voltages applied to the top and bottom crossing wires, forming a bit at each nanowire crossing.

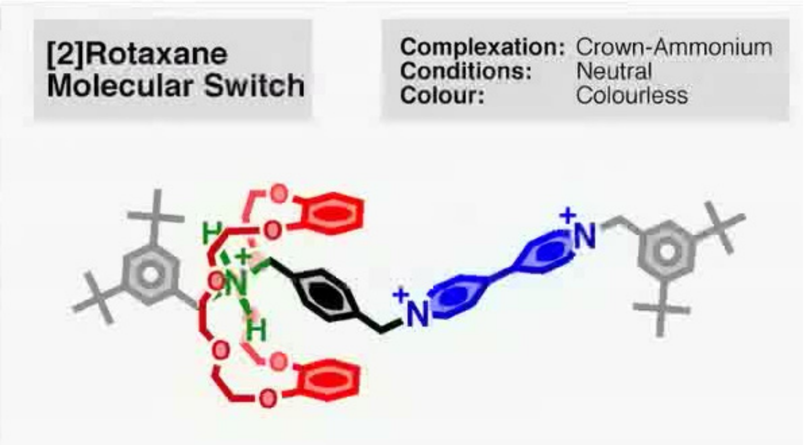


Fig. 3 The molecular organic switch based on rotaxane molecule.

Each bit in the device consists of a silicon and a titanium crossbar with around 100 rotaxane molecules filling in the space between them at perpendicular angles. The hydrophilic diethylene glycol stopper on the left (gray) is specifically designed to anchor to silicon wire (made hydrophilic by phosphorus doping) while the hydrophobic tetraarylmethane stopper on the right does the same to the likewise hydrophobic titanium wire. In the ground state of the switch, the paraquat ring is located around a tetrathiafulvalene unit (in red) but it moves to the dioxynapthyl unit (in green) when the fulvalene unit is oxidized by application of a current. When the fulvalene is reduced back a metastable high conductance '1' state is formed which relaxes back to the ground state with a chemical half-life of around one hour. These nanosystems operate at a scale ranging from 1 nanometer - about one-billionth of a meter - to a few hundred nanometers. For the sake of comparison, the DNA molecule is 2 nm wide, a red blood cell is 2,000 nm and a human hair is 20,000 nm wide.

An other organic switches, the photochromic compounds, are able to switch between electronic configurations when irradiated by light of a specific wavelength. Each state has a specific absorption maximum which can be read out by UV-VIS spectroscopy. Members of this class include azobenzenes, diarylethenes, dithienylethenes, fulgides, stilbenes, spiropyrans and phenoxynaphthacene quinones.

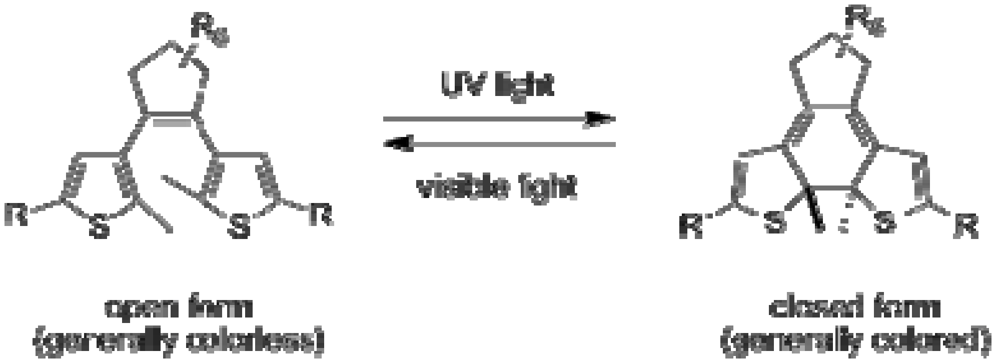


Fig. 4. The molecular switch in photochromic organic materials (the photochromic commuton)

The organic chemistry discovered recently an impressive number of molecules wich are able to be used in switching devices because they are sensitive to various kind of radiations, to electrical field and even to chemical environment. The minimum unit for switching can vary from one molecule to a large group of molecules.

4. The switching in phase-change materials (crystalline *commuton*)

The most promising media for rewritable applications are the so-called "phase-change materials". The idea to use an amorphous-crystalline phase transitions for information storage dates back to the 1960s when Stanford R.Ovshinsky suggested a memory switch based on changes in the properties of amorphous and crystalline phases of multi-component chalcogenides [1]. In the new switches the amorphous as-deposited $Ge_2Sb_2Te_5$ layer is crystallized by exposure to a laser beam of high intensity to heat the material to a temperatures slightly above the T_g. A subsequent exposure to an intense and short laser pulse melts the material that is then converted into the amorphous state on quenching. A recorded bit is an amorphized mark against the crystalline background.

The process is reversible and this is essential for a rewritable memory. Strand et al. [9] have shown that in Ge-Te alloys having non-stoichiometric atomic ratios occurs phase separation during crystallization: $Te_{50}Ge_{50}$ phase and pure crystalline tellurium or germanium are formed. The limitation of the crystallization rate is given by this slow process of phase segregation. Phase segregation during crystallization of non-stoichiometric Ge-Te can be avoided by adding antimony to samples having tellurium concentration from 45 to 55 at.% over a wide range of Ge:Sb ratios. These alloys exhibit laser induced crystallization time of less than 50 ns. Kolobov et al. [9] have shown the angström-scale mechanism of structural phase-change in materials, on the case of Ge-Sb-Te chalcogenide.

In Fig. 5 (after [9]), it is shown the germanium atom in the f.c.c. structure formed by tellurium atoms. The germanium atoms occupy the octahedral and tetrahedral symmetry positions in the crystalline and amorphous state, respectively. The strong covalent bonds are shown with thicker lines than the weak bonds (Fig. 5a). An intense laser pulse induces the rupture of the weak bonds and the germanium atom flips into the tetrahedral position (Fig. 5b). An alternative description of the structural transformation on melting is an umbrella flip distortion resulting in the disordering of the germanium sub-lattice. It is remarkable that the covalent bonds remain intact. The authors conclude that Ge-Sb-Te can be viewed as being built from well-defined rigid building blocks of composition $Ge_2Sb_2Te_5$. In the crystalline state, the constraint of the mutual arrangement of the building blocks in space is such that tellurium atoms form a f.c.c. lattice. Inter-block interaction and long-range ordering cause the resulting structure to resemble the rock-salt structure. In the amorphous state, inter-block interaction is weakened, which allows the block structure to relax so that the bonds shrink and germanium umbrella flips into its preferred tetrahedral coordination.

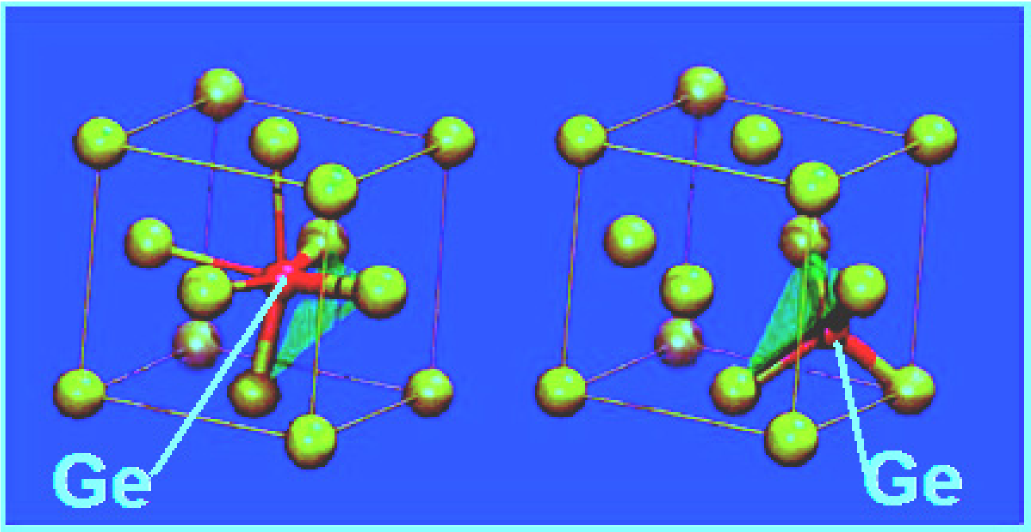


Fig. 5. Local structure of Ge-Sb-Te around germanium atoms in the crystalline (left) and amorphous (right) states [9. (Courtesy of A. S. Kolobov)]

The results presented in [10] provide a clear explanation as to why switching in Ge-Sb-Te is fast and stable and point out the power of angström-science (angström-scale phenomena). The crystallization – amorphization process does not require the rupture of strong covalent bonds and the transition is diffusionless. The fact that the tellurium sublattice is partially preserved, as well as that of the conservation of the positions of the antimony atoms, explain why the transformation can be easily reversed. Bond rupture is believed to be due, at least partially, to electronic excitation. It should be noted that the amorphous structure, at least on a local level, is well defined, thus enhancing the reversibility of the transition.

5. The switching in amorphous materials (amorphous *commuton*)

The smallest cluster in the binary amorphous chalcogenide (As_2S_3) that exhibits two different metastable states is the cluster with 20 atoms: As_8S_{12}. In Fig. 6 is shown the As_8S_{12} cluster in two configurations. In both clusters half As atoms are situated outside and half inside the cluster. The clusters differ by the orientation of S atoms. In the first cluster only 2 S atoms are situated within the cluster and 10 S atoms are oriented outside the cluster. The cluster differs not only by geometrical configuration but also by their free energy: 33.92 meV and 10.16 meV, respectively. To switch from one metastable state to the other stable state, the cluster must overcome a certain potential barrier. A higher barrier is characteristic for the reverse transition.

Different excitation thresholds are necessary to basculate the cluster forth and back. In the low energy configuration the bonding angles in the cluster (after relaxation) are situated in the vicinity of the angles known from the crystallo-chemistry of the compounds with Ge, Sb, and Te, while in the high energy configuration the bonding angles are dispersed over a range of angles of ~ 25°.

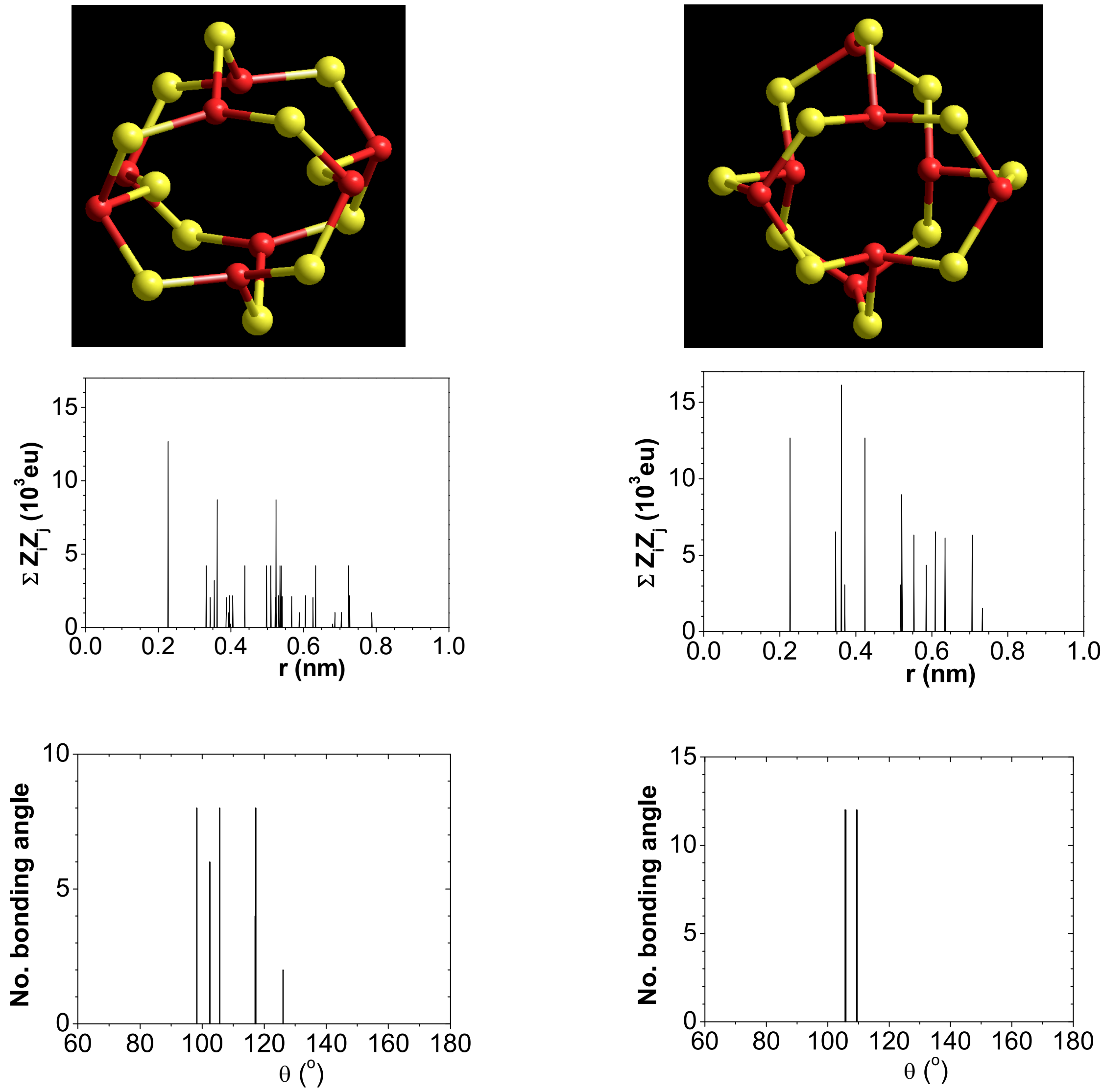
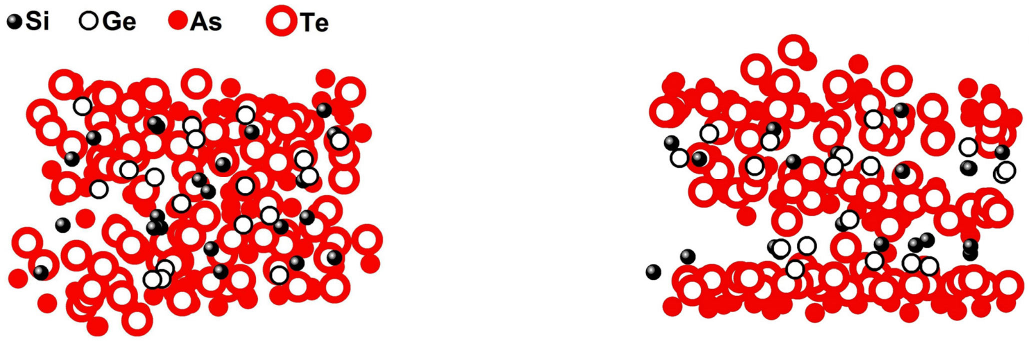


Fig. 6. Two possible configurations for the As_8S_{12} *cluster:*
a. 2 S atoms are situated within the cluster and 10 S atoms are oriented outside the cluster; total free energy = 33.92 meV (Free energy / (bond and angle) = 0.945 meV);
b. all 12 S atoms are oriented outside the cluster; total free energy = 10.16 meV (Free energy / (bond and angle) = 0.283 meV);
In both clusters half As atoms are situated outside and half inside the cluster.

The structure of the quaternary glass $As_{30}Te_{48}Si_{12}Ge_{10}$ seems to be given by a random network of atoms linked by covalent bonds. The atoms retain the covalent character known from their crystalline compounds. The As-Te bonds are favoured. The composition with 30 As and 48 Te, approaching As_2Te_3 composition, supports the idea that the main configuration in this glass is based on As_2Te_3 layers. Therefore, the idea to embed Si and Ge in As_2Te_3 layers is attractive. Interconnection of the As_2Te_3 layers containing Si and Ge atoms is possible if Si(Ge)-Te-Si(Ge)bonds are considered in-between the layers. The phase change under heat consists in the separation of the layers by breaking the interlayer bonding and releasing of Ge and Si out of the As_2Te_3 layers. Thus, the new phase becomes more ordered and more stable than the initial phase.

A return back to the former glassy phase is possible only by strong excitation (melting) followed by quenching.



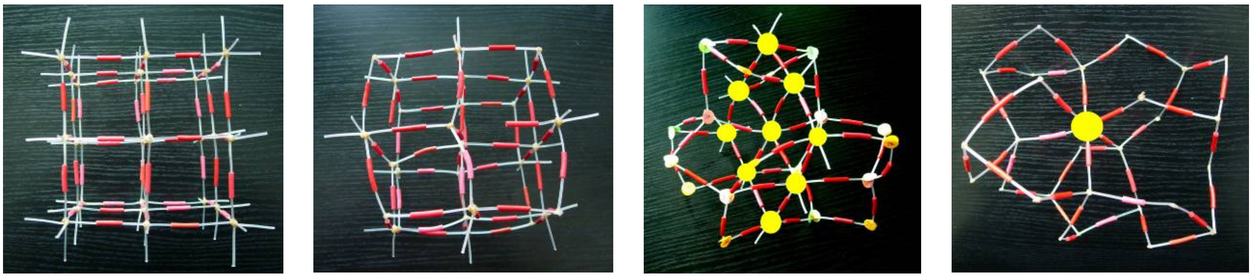
a b

Fig. 7. Model of $As_{30}Te_{48}Si_{12}Ge_{10}$ glass (a) and the model of a new amorphous phase got by structural transformation (b).

The nanometer-scale model consists in an arrangement of three disordered layers of type As_2Te_3. These layers are doped randomly with Si and Ge. The physical model made of plastic units has 202 atoms. Silicon and germanium take the places of tellurium atoms. They bind two neighbouring layers though the intermediation of the tellurium atoms released from the bonds occupied by Ge or Si. Thus, two disordered As_2Te_3 type layers are linked by square bridges Si-Te-Si(Ge)-Te. The model was relaxed by computer using the standard Monte-Carlo – Metropolis procedure and appropriate force constants. The results are shown in Fig. 7a [10]. In the following step we modeled the phase transformation induced by external factors acting on the glass. The excitation of the stressed bonds in the glass leads to the breaking and reforming of the bonds in a new configuration. The bond breaking between disordered layers is most probably due to stressed bonds Si-Te and Ge-Te. Tellurium takes the place of Ge (or Si) in the layers and forms strong As-Te bonds that fit the network of type As_2Te_3. The remaining Si and Ge atoms form separated dimmers or small clusters outside the As_2Te_3 domains. The atomic scale model of the new phase, relaxed by computer is shown in Fig. 7b.

6. The minimum cluster that supports the switching properties in phase change materials based on Ge-Sb-Te

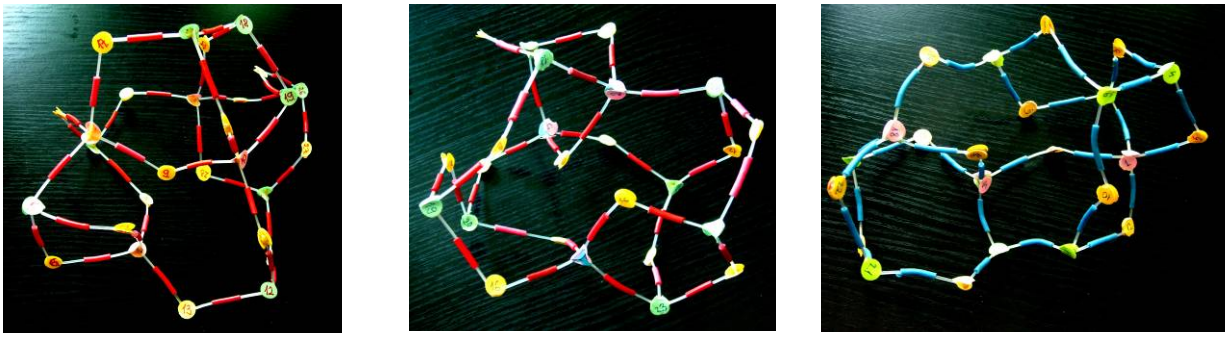
We have modeled the transition from a crystallite to an amorphous cluster in Ge-Sb-Te phase change material. Fig. 8 a-d shows the stages of reversible transformations by gradually changing the atom bonding from octahedral configuration specific to crystal (cubical, spinel-type) to the disordered, amorphous cluster characterized by normal bonding of the elements (4 for Germanium, 3 for Antimony and 2 for Tellurium). In the last stage corresponding to fully amorphous phase of the cluster we got several configurations.



a b c d

Fig. 8. The switching cluster (commuton) in Ge-Sb-Te chalcogenide material

The yellow spots on Fig. 8c and Fig. 8d are showing the reminiscent crystalline feature, which vanishes step-by-step.



a b c

Fig. 9 Amorphous clusters

The modeling of the basical switching unit in Ge-Sb-Te memory material shows that a minimum unity of 27 atoms (a complete large cube with the composition of the material) seems to be the basic switching unit (the Commuton) in this class of materials of great perspectives for applications in smart memory devices.

The starting unit is strictly crystalline and unique, while the disordered phase is multiple. We suppose that cycling of the commuton does not determine the strict recovery of the crystalline phase, but only a partially ordered phase. In such a case we can easily explain why the speed of switching is very high: the changing of the atomic configuration is produced with limited positional changing, thus the transition, based especially on the transition of the quality of the chemical bonds, is easier, while the electrical and optical properties suffer an abrupt change.

7. Conclusions

We have shown that in many switching materials could be defined a minimum unity of switching, based on the properties of atoms, molecules or clusters of atoms (molecules) with specific properties, related to changes in chemical bonds. The minimum unit that defines the switching properties of a material was called “commuton”.

Acknowledgement

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