Switching mechanism in amorphous chalcogenides

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Abstract. The electrical switching in solid compositions based on chalcogenide materials is discussed. Different mechanisms proposed for switching effect are reviewed. A new description of the switching phenomenon is done. The switching is regarded as due to formation and breaking of the links between the dendrites of crystalline nuclei in bulk materials, as a consequence of the energy pumped by an electrical field. This mechanism explains the very short switching time (<20ns), the possibility to get smart memories based on multisteps of resistivity and the high number of cycles supported by the cell ($10^{16}$).

1. Introduction
The memory effect in solid state has been a great challenge along the last decades. One of the leading class of materials where the switching phenomenon was discovered by Ovshinsky in 1968, is the class of chalcogenides. Various combinations of chemical elements including or not the chalcogenide ones have been prepared and tested regarding the switching effect. Multistep switching has been discovered recently and this opened the way toward intelligent memories.

In spite of large scale investigation of the switching effect in solids, the mechanism of switching is not fully understood. This is due to a variety of phenomena that are produced into a material when subjected to an electrical or optical field of excitation.

2. Resistance change versus charge storage
Traditional memory technologies are rapidly approaching miniaturization limits as the industry moves toward memory cells with 22-nm lateral features projected for 2016. The reason is that they are based on charge storage and it becomes increasingly difficult to reliably retain sufficient electrons in these shrinking cells. Magnetic and ferroelectric random-access memories, which are currently used in niche markets, share this struggle with scaling.

Nonvolatile memory concepts aimed at the horizon beyond 2013 are based on resistance change rather than charge storage.

The phase-change memory in chalcogenides, is based on change from crystalline to amorphous state and back: the crystalline state (on state, low resistivity state) is well known in many chalcogenides and for some systems, as e.g. Ge-Sb-Te, is characerized by very low (metallic) conductivity and high optical reflectivity. The amorphous state (off state, high resistivity state) is characterized by high resistivity and low optical reflectivity. The transition between these two states with very different properties is the basis of the phase-change memory used in modern switching applications.
3. Switching mechanism in electrolyte based memory cells

The first cell memory in solid electrolytes (programmable-metallization-PMC memory cell) has been obtained and investigated by Mitkova et al [1]. The basic material was 50 nm thick Ag doped Ge-Se film. The principle of working is the diffusion of silver in a chalcogenide material. During PMC cell operation it occurs the formation and removal of Ag-deposit through of an electrolyte amorphous medium. A sketch of the mechanism of switching stages is given in figure 1.

**Figure 1.** The mechanism of switching in a memory cell based on the diffusion of Ag in a chalcogenide electrolyte (Ge-Se): a) writing step (A very small voltage rapidly injects excess silver ions into the electrolyte, to form silver dendrites on cathode); b) erasing step (A **very small** reverse voltage removes excess silver from the electrolyte, excess silver is **backed** on the silver electrode)

The usual materials (electrolytes) used by various companies in making memory cells based on the above described principle are:
There are also cells with resistivity-change memory based on transition-metal oxides. The cells work by the diffusion of metals into the oxide structures under the influence of an electrical field. The resistivity can be changed in a reversible way as a function of the electrical field polarity. Thus a reversible memory can be obtained. The systems investigated up to day are:

- Metal doped WO$_3$,
- Metal doped SiO$_2$.

4. The electrical switching mechanisms

4.1. The old views on the electrical switching mechanism in chalcogenides. The thermal switching and filamentary discharge.

The observation of switching in thin semiconducting chalcogenide films goes back over a considerable period. Since Ovshinsky reported in 1968 [2], threshold processes in thin layers of chalcogenide glass alloys there was a lot of attempts to explain these observations. The problem is still challenging. Several scientists collected arguments to demonstrate that the switching is essentially thermal, the current in the ON state being carried by a hot filament. Others, as Adler et all [3], presented an electronic interpretation of the phenomenon.

![Figure 2 a. The electrical discharge into an insulating material (here in air).](image)

Thermal theory predicts ON-state “filament temperature” of the order of several hundreds degrees centigrade, depending on the assumptions made [4, 5], whereas the glass transition temperatures of the multicomponent chalcogenide alloys generally used for threshold switches are in the range 150 – 350 °C. This leads to an expectation of gross instability, whereas the threshold switches are in fact highly stable (more than $10^{14}$ operations under pulse conditions). Step by step it has become clear that the ON-state channel in thin chalcogenide switches is not ordinarily hot and this is a strong evidence against a thermal model. Although the early theories attempted to reduce the switching effect to heating of the sample (as a whole or in the filament), later studies revealed that heating plays an insignificant role in reversible switching. It has been accepted that heating provides some
contribution only to the switching delay time after the threshold field strength has been reached, as well as to the formation of memory and to the structural transformation of the material. Regarding the filamentary source of switching, the conducting channel is similar to the shape of an electrical discharge between two electrodes and through an insulating material (polymeric or not), (see figure 2a). In the PMC the Ag filaments exhibit a dendritic structure (figure 2b).

The application of sufficiently high electric fields to any material eventually results in deviations from linearity in the observed current – voltage characteristics. There are two general classes of explanations of such non-ohmic effects: thermal and electronic.

The thermal effects arise because the electrons accelerated by the field always emit phonons in an attempt to return to equilibrium. Electronic effects are due to changes in the response of the charged carriers to high applied fields. In general both effects must be considered in any theoretical analysis [6]. As a conclusion, the switching in chalcogenide glasses has particularly desirable properties because of the flexibility resulting from the presence of lone-pair valence electrons while at the same time lead to a large density of valence alternation pairs.

The switching phenomena follow from electronic effects, threshold switches from the field stripping of chalcogen lone-pair electrons and subsequent filled of lone-pair induced traps, while memory switching results from local structural rearrangements in less cross-linked chalcogenides under excitation conditions.

4.2 The electronic mechanism. The two level system.

The analysis of many papers [7] has shown that switching is produced by the following mechanism: the electric field generates free electrons and holes and this generation is most pronounced at the threshold field strength. These electrons and holes fill the traps. After all the traps have been filled, the resistance decreases sharply and switching occurs. Nevertheless, a high number of problems remain unclear: the nature of the traps, why the efficiency of trapping is maximum at the threshold field. No quantitative results are available. Different authors proposed different defects as traps: valence alternation pairs, dangling bonds, two-level systems.

Chaban [8] studied the glass transition and elaborated a model for this transition. According to Chaban’s theory the glass transition point is the temperature at which ordered regions start to come in contact. This definition provides an explanation for the jumps of the heat capacity and other quantities at the glass transition point. The smallest change in heat capacity should correspond to the appearance...
and disappearance of one Frenkel hole in an ordered region. The related discreteness of levels should be observed at low temperatures. This idea has been used by Chaban [9] to built a model of low temperature anomalies in glasses. The ordered regions are characterized by a unique sensitivity to changes in the external conditions. They are sensitive to change of pressure, shear stress or electrical field strength, but also to the orientation of the nuclear spins, to the ejection of electrons from ordered regions by phonons, etc.

Chaban assumes that for adjacent electric field induced localized states of an electron of energy $E_e$ (pseudoexcitonic states) that have one electron each, it is energetically favourable to combine with the formation of a two-level system. The upper and lower levels of this system correspond to parallel and antiparallel spins, respectively. Chaban assumes that the energy difference between these levels is greater than $k_B T$ at room temperature. If the number of these two-level systems is larger than the percolation threshold, singlet electron pairs will be able to move throughout the sample in a resonant non-dissipative manner over the paths created by overlapping wave functions of these systems. Switching corresponds to the transition to a new type of conduction where the electrons propagate mostly through non-dissipative paths.

4.3. The flip-flop mechanism.
Kolobov et all[10] discussed this mechanism in the particular case of Ge-Sb-Te material, the structure of the crystalline phase is similar to the rock salt structure with a rather stable Te face-centered cubic (fcc) sublattice. Due to difference in covalent radii of the constituent species, Ge, and to a lesser extent Sb, are shifted from their corresponding fcc sublattice sites giving rise to a system of shorter bonds (stronger) and longer bonds (weaker). The shorter bonds are more rigid and thus provide a framework for the local structure. The germanium bonds (four) remain intact during transformation to amorphous state and thus the medium is fast and stable.

The rupture of the weaker bonds in GST (Ge-Te bonds) produces a net force on Ge atoms that makes it move along the [111] direction across the Te 111 plane. Provided the energy released by the bond relaxation is sufficient to overcome the energy barrier due to repulsion by Te atoms, Ge can flip across the plane in a tetrahedral site (figure 3).

The structural transformation consists in the switching of the Ge atoms between octahedral sites and tetrahedral sites due to the presence of strained Ge-Te bonds. Such mechanism seems to be common in binary Ge-Te and in quasi-binary GeSb$_2$Te$_4$ [10].

4.4. Switching in multistage memory materials. Nucleation and growth.
Phase change materials mainly include two families of materials: nucleation – dominated chalcogenide alloys and growth dominated chalcogenides alloys. In the first category enter GeTe –
Sb$_2$Te$_3$ alloys in which the crystallization is controlled by nucleation of crystallites. In the second category enter the In and Ag doped Sb$_2$Te$_3$ alloys in which crystallization occurs by motion of a glass-crystal interface [8].

4.4.1. Growth of the nuclei without dendrites. Existing models describing the crystallization behaviour of phase-change materials using optical and electrical memories are based on classical theory of nucleation. The values of the parameters: viscosity, diffusivity, fusion enthalpy must be estimated. The normal memory effect is produced in the thin memory film by nucleation of crystalline germs and growth rapidly as dendrite development. The multistate must be related to the variable number of dendrite filaments across the chalcogenide material.

Crystallization often starts with the formation of small, unstable clusters of a new phase. Eventually some clusters reach a critical size beyond which they are stable, such that they can grow rather than dissolve. Homogeneous nucleation occurs at a random position in the original phase, while heterogeneous nucleation takes place at preferential sites as surfaces, interfaces and impurities. As a function of the material type and preparation parameters the nuclei can grow without dendrites. In such a case the time of switching is considerably slower.

When the phase change is produced the nuclei must reorganize or develops in order to create percolation paths. In the case of non-dendritic development the percolation is considerable delayed. This is because the neighbouring nuclei are in a limited number and the probability of sticking and making crystalline paths is lower.

Figure 4 shows an image of As$_2$S$_3$ glass deposited. The round configurations grow without developing dendrites.

Figure 4. As$_2$S$_3$ deposit which grows in size without developing dendrites. The density of nuclei remains unchanged.

Figure 5. a) growth of the crystalline phase by size increase of crystallites, b) growth of the crystalline phase by multiplication of the crystallites and a moderate growth of crystallite size.

Figure 5 is a sketch of crystallization advancement in a amorphous material in two ways.
a) growth of the crystalline phase by size increase of initial nuclei,
b) growth of the crystalline phase by multiplication of the nuclei and a moderate increase in size.

The rigorous treatment of transient effects (e.g. transient nucleation rate case a) has been developed by Kashchiev et al. [13]. He has proposed the nucleation rate for isothermal annealing conditions to be:

\[ I(t) = I_{ss} \left( \frac{4\pi}{r} \right)^{1/2} \exp \left( -\frac{\pi^2 t}{4r} \right), \]

where \( I(t) \) is the nucleation rate (cm\(^{-3}\)s\(^{-1}\)) and \( t \) is the time of material annealing.

This function is plotted in figure 6 as a function of time for 250 °C, the incubation is \( \sim 2 \) ms much higher than the time of switching.

![Figure 6](image)

**Figure 6.** Transient nucleation rate of GST as a function of time for 250 °C [15] (case a).

The growth rate of crystalline clusters (case b) is plotted versus temperature in Fig.7. The process is described by the following equation:

\[ \frac{dn}{dt} = g(n) - d(n) \]

where both the growth and dissolution rate is taken into account.

The growth rate is higher for higher temperatures but usually is situated in the range of \( 10^{-4} \sim 10^{-2} \) cm/s (\( 10^{3} \) nm/s \( \sim 10^{5} \) nm/s). Usually, time of switching is 20 ns and the growth of nuclei is up to \( 2 \times 10^{-5} \sim 2 \times 10^{-3} \) nm.

In the case of memory switching, the ON state is triggered when the power is large enough to promote crystallization (\( T>T_c \)) but low enough to avoid melting of the conduction filament (\( T<T_m \)) at the end of the pulse, when power density is higher than that corresponding to \( T_m \), then a transition to OFF state occurs.

4.4.2. Growth of the nuclei with dendrites. After spontaneous formation of nuclei, further growth of these small crystalline clusters develops with more or less extension of the dendrite as a function of various parameters of the material. A typical material that shows dendrite crystallization is Sb\(_2\)S\(_3\). As function of the deposition parameters many other amorphous materials develop crystallites with dendrites.
Figure 8 shows the development of nuclei with long dendrites. These dendrites can occasionally meet and form thus a short conduction channel. This is a simple mechanism for the formation of a conducting channel into the material. The first step before switching under the action of an electrical field, in the amorphous materials are nucleation of small crystalline islands that grow and develop dendrites. The switching in material occurs when the dendrites become linked so that a percolation path appears (figure 8a - state ON). To go back a new pulse of the energy removes the inter-dendrite linkage and the percolation paths are destroyed. Thus state OFF is triggered (figure 8b).

Crystalline dendrites develop during the growth of many thin solid films, as e.g. As₂S₃. This is illustrated in figure 9.

4.5. Multi stage switching.

The most prominent and widespread use of chalcogenide materials is in the rewritable phase-change optical memory disks and in rewritable digital versatile disks. Both optical and electrical data storage rely on the reversible phase transformation between amorphous and poly-crystalline states. On optical disks data recording is achieved by writing an amorphous dot on a crystalline film by local melting with a focused laser beam. When the laser is switched off, rapid quenching of the melt leads to amorphization of the dot. Since an amorphous dot has a lower reflectivity than the surrounding crystalline background, the written bit can be read by a low power laser. Conversely, erasing the dot is achieved by heating the amorphous dot at temperatures less than melting point and allowing the amorphous dot to crystallize. Crystallization is much slower than amorphization.
Electrical memory uses the same two states of the chalcogenide material. A small volume of PC material is transformed by applying current pulses. Resistive heating are produced. Crystallization is initiated by a pulse heating. The state of the memory cell is read-out non-destructively by measuring the resistivity caused by the current pulse. The amorphous phase is obtained by a pulse sufficiently large to achieve melting. Subsequently, a rapid quenching allows the material to become amorphous. The crystalline phase is the low resistivity state (state ON). The amorphous phase is high resistivity state (state OFF). High speed crystallization is important. Therefore, phase separation is detrimental to short switching time. Moreover the atoms must not move on large distances. That is why only special materials as for example Ge-Sb-Te are recommended for switching.

The old materials based on Ge-Sb-Te-S suffer phase segregation [11] upon crystallization. The new materials based on Ge-Sb-Te exhibit congruent crystallization characterized by no phase segregation and rapid crystallization in ~ 20 ns. The life time of the switching is 10 years at 110 °C.

As a function of the material type and preparation parameters the nuclei can grow without dendrites. In such a case the time of switching is considerably higher. When the phase change is produced the nuclei must reorganize or develop in order to create percolation paths. In the case of non-dendritic development the percolation is considerable delayed. This is because the neighbouring nuclei are in a limited number and the probability of sticking and making crystalline paths is lower. When the nuclei develop by dendritic growth, the percolation threshold is reached more rapidly. When nuclei grow by dendrite extension, every nucleus becomes in contact with a higher number of neighbours.

As in the case of neuronal systems, a huge amount of conexions between cells determines a very good connectivity. Therefore the percolation can be attained easily. To block completely the crystalline continuity it is necessary to block the connection at random for a great amount of dendrites.

While the percolation limits in systems of lattice points of given symmetry are high and vary in broad range (from 0.20 to 0.43), in dendrite connected networks the percolation threshold can be considerably lower (down to 0.14 for taking into account the effect of the next nearest neighbours, or even 0.10 when next-next-nearest neighbours are considered).

The multistage memory makes use of new mechanisms in the deceptively simple, single, amorphous nano-dimensional spot in the low current operational regime. As current pulses are applied minute nanocrystalline region form and the volume fraction of such crystalline phases increases with each current pulse. Crystallization can occur through nucleation/growth upon the application of a current pulse. The microcrystallites generated by a sequence of pulses form a temporarily coherent sequence of states.

Figure 10 shows the multistage electrical switching in a chalcogenide material.

![Figure 10](image)

**Figure 10.** Programming energy changed by changing power at constant time during multistage switching.

The connection by dendrite explains the following properties of multiswitching:

a) the very low aging and the stability of the switching parameters in time,
b) the very short time of switching.

The switching effect is flexible because the percolation during switching to stable ON state is easily reached. For dendrite growth of conducting nuclei the percolation threshold is much lower. For passing to the state OFF it is enough to melt only the dendrite thin contacts and not all the crystalline part. Thus the rate of switching to OFF state is higher. In the same time multi-state stable switching can be obtained.

The nano-crystallites are distributed randomly throughout the chalcogenide material. As they grow, a percolation path results, a continuous, high conductivity pathway across the material between the contacts. The increment of the crystallization that occurs upon application of a current pulse is dictated by the energy deposited by the pulse into the material. Once the energy is accumulated a new state occurs. The crystallites are developed up to a given dimension and spatial extension. This is in close analogy with neurosynaptic functionality in brain. Continued application of energy to a given structural state induces additional crystallization and further accumulation of energy until sufficient energy has been applied to reach the percolation transition. The energy required for percolation is the threshold from a high resistance state (state OFF) to a low resistance state (state ON). In the multistage memories based on optical mechanism, we must replace the resistance with reflectivity.

It seems the process is analogous with that produced in neuronal networks. Firstly, energy accumulates at a neuron through dendrites that link through synapses to other neurons. At a certain level of energy (a threshold energy) the neuron fires: This means a discharge is produced and the energy is transferred to other neurons. In the multi-stage device, the abrupt reduction in resistance that occurs at the percolation transition is analogous to the firing of a biological neuron.

A chalcogenide device with natural oxide on its electrodes exhibits some unique switching and memory behaviours. I-V characteristics showed a reversible bias-polarity-dependent switching behaviour via some intermediary states. Device resistance as a function of pulse height and decay behaviour from a low resistance state revealed that there were some intermediate states which were relatively stable in a certain voltage range and a certain period. These relatively stable intermediate resistance states make multi-state storage possible. These multi-states might be related to the number of dendrite filaments across the chalcogenide channel which could be induced by electrical pulses.

Regarding the importance of the material for multi-stage processes, it is remarkable the role played by Sb$_2$Te$_3$. A comparative study of crystallization processes in Sb$_2$Te$_3$ films using laser and thermal annealing techniques has been carried out by Reddy et al [12]. Usually the crystallization of this material is produced by developing long dendritic configuration. Adherent and pin-hole free amorphous Sb$_2$Te$_3$ thin films have been obtained by vacuum evaporation at substrate temperatures of ≤25 °C. The films have been crystallized by thermal and laser annealing, and the crystallization processes monitored as a function of annealing temperature and laser scan speed. A comparative study of topography reveals disk-shaped crystallized areas in thermal crystallization and dendrite growth in the laser induced process. The crystallized films in both cases contain a single Sb$_2$Te$_3$ phase. Activation energy of 2 eV for crystallization, determined using differential scanning calorimetry indicates good room temperature stability of the amorphous states.

In Ge-Sb-Te the short range order is almost the same in the amorphous phase and in the corresponding crystalline one. The local order already present in the amorphous phase is likely responsible for the fast crystallization process (100 ns, while in GeTe is 300 ns). The phase change is completed without appreciable atomic movement. In binary system the local atomic order is different in crystalline and amorphous phase. In the amorphous state the germanium atoms are fourfold coordinated by 2 Te and 2 Ge atoms. When crystallization occurs the Ge-Ge bonds disappear and Ge atoms are uniquely surrounded by Te atoms. The phase transformation from amorphous to crystalline state requires the destruction of the Ge-Ge bonds and a significant movement of the Ge atoms to join the crystalline sites. These processes limit probably the crystallization speed and, therefore, the switching rate.

5. Mechanism of switching with fractal growth and dendrite interaction
The fractal growth of crystalline nuclei is the key factor of the rapid transition between the conducting and insulating state. In the same time the multistage memory can be easily explained. The crystalline nuclei are formed in the bulk amorphous matrix with various density and sizes.

As opposite to the old model with dendrite extending from one electrode to the other, the new model implies the formation of randomly distributed crystalline clusters that grow with dendrite development. These dendrites determine a higher probability to form percolation paths due to multiple possibilities to interconnect various developed nuclei. This is similar to the neuronal connections. The intricate connexions by synapses and long dendrites makes the connectivity much more complex than in the case of simple networks of atoms with simple geometry.

The mathematical percolation thresholds calculated for various lattices are given in table 1.

**Table 1.** Mathematical percolation thresholds in 3d lattices.

| Lattice                         | Z   | Site Percolation Threshold | Bond Percolation Threshold |
|--------------------------------|-----|----------------------------|----------------------------|
| Ice                            | 4   | 0.433 (11)                 | 0.388 (10)                 |
| Diamond                        | 4   | 0.426 (+0.08,-0.02)        | 0.390 (11), 0.3893 (2)     |
| Simple cubic                   |     | 0.3116                     | 0.2488126 (5), 0.2488125 (25) |
| Icosahedral Penrose            | 6 (average) | 0.285              | 0.225                      |
| Penrose w/2 diagonals          | 6.764 (average) | 0.27               | 0.207                      |
| bcc                            | 8   | 0.2459615 (10)             | 0.1802875 (10)             |
| fcc                            | 12  | 0.1992365 (10)             | 0.1201635 (10)             |
| hcp                            | 12  | 0.1992555 (10)             | 0.1201640 (10)             |
| La$_{2-x}$ Sr$_x$ Cu O$_4$     | 12  | 0.199272 (2)               |                            |
| Penrose w/8 diagonals          | 12.764 (average) | 0.188              | 0.111                      |
| cubic with n.n.n.              | 18  | 0.13735 (5)                |                            |
| simple cubic with short-length correlation | 6+ | 0.126 (1) |
| cubic with n.n.n.              | 26  | 0.0976445 (10)             |                            |

n.n.n. = next-nearest neighbor, n.n.n.n. = next-next nearest neighbor

In the case of the spatial network of points the percolation threshold depends on the number of first neighbours. For spatial lattices with 4 neighbours (diamond) the percolation threshold is 0.43. For hcp lattice with 12 neighbours the percolation threshold is 0.20. for percolation if one takes into consideration the next nearest neighbours in the cubic lattice (18) the percolation threshold is 0.137. When one considers the percolation taking into account the next-next nearest neighbours, as in cubic lattice: 26 neighbours, the percolation threshold is 0.098.

In the new model the memory process occuring in a chalogenide film is as follows:
- Two dendrites develop closely one to another.
- The dendrites can link at certain points and make a continuous channel of crystalline phase from one electrode to another (this is the ON-state).
- During a higher electrical pulse the dendrites are partially melted and the thinner zones of contact disappear (this is the OFF-state), the conductivity drops abruptly because the thin dendrite connections are destroyed.
- A new electrical pulse determines a new crystallization process with the formation of new bridges, and therefore new percolation paths.

What is important is the role played by the nuclei with dendrites. This is similar to the dendrite action in neuronal cells.
By accumulation of energy the nuclei can fire, as in the case of neurons, i.e. the energy is transferred primarily to dendrite who links one nucleus to another and can form or break the path between nuclei and thus the state ON or the state OFF of the circuit is triggered.

The dendrites are extending at long distances in-between the fundamental crystallites. Thus a crystallite can form channels to another crystallite situated not only in the first neighborhood but also in the next-next neighborhood and even farther. Thus the multiple possibilities to connect the crystalline nuclei, makes the percolation path to be achieved easier. Thus, as shown above, the percolation threshold can be very low and, therefore, the threshold condition is considerably easier to get and needs a lower amount of energy. Moreover, the energy supply needed for amorphization of the thin dendrite contacts is very low.

6. Discussion
Optical memory in the same class of chalcogenides is a big challenge for the electrical memory, because it is simple and can be used with simple devices (optical disks) already existent. The best materials belong to the class: Ge-Sb-Te. They are intended to replace the non-volatile flash memories.

Their main characteristics are:
- The commercial Optical Storage Media are based on Ge-Sb-Te chalcogenides,
- The materials are based on changes in structural configurations,
- The materials exhibit high Optical / Resistive Contrast,
- The switching characteristics can be very different. They depend strongly on the type of materials,

All these memories are in principle related to the electronic states in the chalcogenides

The multiscnitching effect is based on configurational changes in the material: from amorphous state to intermediate states and crystalline states and back by careful operation.

Why the chalcogenides are the best materials for switching? Firstly chalcogenide materials are highly resistive despite the presence of defect and impurities. This is because the VAP defects pin the Fermi level near the gap center. This property gives a high resistive OFF state. This is totally different from the other semiconductors with comparable gaps. Secondly, the chalcogenides can easily and quickly undergo reversible structural transitions between amorphous and crystalline states. Thirdly, the chalcogenides are materials that undergo phase change with minimum motion of the constituent atoms. Thus the switching rate is high. Switching materials based on diffusion and phase separation are not appropriate because the switching is very slow due to low rate of processes implied.

7. Conclusions
The switching phenomenon is very important for modern optoelectronics. The chalcogenides are master materials for both electrical and optical switching.

Various switching mechanisms at the atomic scale have been proposed up to day.

The newest and the most subtle one is based on the formation of the pre percolation stage where the crystalline nuclei are grown with extended dendrites in an electric field or photo-excitation. More energy determines more spatial extention of the dendritic structure, accompanied by random linking of dendrites giving rise to the percolation path between electrodes (state ON). The OFF state appers when the excess of energy pumped in the system is enough to melt the narrow dendrite connections and to wipe out the percolation paths.

References
[1] Mitkova M and Kozicki M N, 2004 Non-Crystalline Materials for Optoelectronics (Series: Optoelectronic Materials and Devices ) v 1 ch. 8 pp 211-258
[2] Ovshinsky S R 1968 Phys. Rev. Lett. 21 1450
[3] Adler D, Henisch H K and Ovshinsky S R 1978 Rev. Modern Physics 50
[4] Popescu C and Croitoru N 1972 J. Non-Cryst. Solids 8-10 531
[5] Popescu C 1975 Solid State Electron. 18 671
[6] Adler D, Shur M S, Silver M and Ovshinsky S R 1980 J. Appl. Phys. 51 3289
[7] Madan M and Shaw M, 1988 The Physics and Applications of Amorphous Semiconductors (San Diego, Ca: Academic Press)
[8] Chaban I A 2007 Physics of Solid State 49 420
[9] Chaban I A 1979 Fiz. Tverd. Tela 21 1444
[10] Kolobov A V, Fans P and Taninaga J 2005 J. Appl. Phys. 44 3345
[11] Njoroge W K and Wuttig M 2001 J. Appl. Phys. 90 3816]
[12] Reddy G B, Dhar A, Malhotra L K and Sharmila E K 1992 Thin Solid Films 220 111
[13] Kashchiev D 1969 Surf. Sci. 14 209
[14] Senkader S and Wright C D 2004 J. Appl. Phys. 95 504