Abstract

In recent years there has been a rapid development of doped metal oxides, because their use in technique turns out as very promising. In 2008 invented new electronic memory device memristor, opens a broad field for research. The perfect theory for describing memristive behavior of memristor is still unknown. In my seminar I presented one of the most promising models that are so far supported good by experiment.
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1 Introduction

Metal oxide thin films were shown for very applicative in last few years. With the invention of memristor, new passiv electric circuit element, in 2008 a lot of studies started to reveal the physics behind its electric characteristics. A lot of models, explaining doped metal oxide conductive properties were proposed. I describe the simplest of these models in my seminar. Described model explains the electric conductance of metal oxide doped with oxygen vacancies. I focused especially on titanium dioxide, that so far turns out as the most appropritet for memrisive devices. [1] This seminar is even more interesting if you first study my first seminar on this theme, titled memristor.[2]

2 Ionic crystal

Metal oxides molecules are bouded to each other with the ionic bond, so they form ionic crystal. Because of the tendency to minimize electrostatic energy such two-atom crystals are arranged in closely pack lattice. There is no free electron in ionic crystal since they are all used for binding. That makes ionic crystal good insulator. The most famous such a crystal is NaCl. All of examples in seminar are made on titanium dioxide because of its promising usefulness.

2.1 Example of ionic crystal - TiO$_2$

Titanium dioxide occurs in many different forms. At ambient conditions the most common form of TiO$_2$ is rutile, sometimes also called titania. Due to a simple synthesis and many other favorable properties, this is the form interesting for development. In the rutile form titanium dioxide has titanium ions arranged in body centered tetragonal Bravais lattice. The Oxygen ions in this crystal form a base centered monoclinic Bravais lattice. If we look on the both atoms at the same time we notice the hexagonal closely pack distribution. There are two titanium and four oxygen atoms in unit cell of rutile. The rutile unit cell is presented on figure 1.

3 Doped ionic crystal

Ionic crystal become really interesting when we doped it with inpururities. Single ion from crystal can be replaced by another ion. Most common impurity is just a missing ion inside the lattice, what is called vacancie. Such a vacancies give a crystal many specific characteristics.
Figure 1: Unit cell of rutile titanium dioxide. Blue spheres represent titanium ions and red spheres represent oxygen ions. Lattice constants are $a = 4.593\, nm$ and $c = 2.958\, nm$.[3]

Figure 2: There is vacancy in unit cell of rutile presented with black colour. We are trying calculate the potential among the line (dashed), connecting the vacancy and its nearest neighbour in $z$ direction. The nearest titanium ions taken in count are bigger.

3.1 Vacancy doped titanium dioxide

Titanium dioxide consists of $-2e_0$ charged oxide ions ($O^{2-}$) and $+4e_0$ charged titanium ions ($Ti^{4+}$), where $e_0$ is elementary charge. If we remove one oxide ion from lattice we get a vacancie in its place, which represents a loss of charge $-2e_0$. Thus the vacancy carries the effective charge of $+2e_0$. Vacancy can move along the crystal by one of neighboring oxygen ions binds to its place and effective it looks like the vacancy changed the place. We can calculate the probability for vacancy to change the place along the $z$ axis. For simplicity we take in count only the nearest neighbors. We calculate the electric potential along the $z$ axis, on the line, connecting vacancy and its nearest oxygen ion in $z$ direction (figure 2).
With use of simple geometry we get the wanted potential.

\[
\Phi(z) = \frac{8e_0}{4\pi\epsilon_0} \left[ \frac{1}{\sqrt{\frac{a^2+c^2}{16} + z^2}} + \frac{1}{\sqrt{\frac{a^2+c^2}{16} + (c-z)^2}} + \frac{1}{\sqrt{\frac{a^2+c^2}{4} + z^2 - cz}} \right] \tag{1}
\]

where \(a\) is length of unit cell among the \(x\) axis and \(c\) is unit cell length among the \(y\) and \(z\) axis. Figure 3 presents the shape of potential.

![Graph showing electrostatic potential in chosen direction](image)

Potential can be approximated with constant potential to easier further calculating. On the vacancy and oxygen ion place potential drops to zero. We get the problem of particle passage through the square barrier. Barrier height \(V_0\) is determined as average of previously obtained potential \(\Phi(z)\). Length of square barrier is of course length \(c\).

\[
V_0 = \frac{1}{c} \int_0^c \Phi(z)dz \tag{2}
\]

Calculated from integral (2), the square barrier height is \(V_0 = 1.42eV\). Only way for oxygen ion to change place is to tunnel through barrier. Because of ion’s huge mass this probability is practically zero at any reachable temperature. I will calculate this probability later. Similar values of barrier height are obtained if we calculate the potential in any direction around the vacancy. This means that the vacancy is well bonded in crystal lattice and is unable to move around it.
3.2 Electric field

Things change dramatically when doped metal oxide crystal is exposed to strong electric field. Electrical potential energy changes when charged particle moves in electric field ($\int Fds = \int Eds$). We wonder, if oxide ion can get so much energy from electric field, that it changes its place on bravais lattice and occupy the place where the vacancy is. If that could happen, we would get an electric current through the crystal. The distance between ion and vacancy is distance $c$. If ion change the place it obtain $\Delta W = eEc = 2e_0Ec$ potential energie. If obtained potential energy is larger than height of barrier $V_0$ between ion and vacancy, the probability for ion to change its place will certainly be nonzero. Needed electric field for particle potential energy of $\Delta W = V_0$ is $E = 0,24V/nm$. With affordable voltage we can get so high electric field only on very small distance ($E = \frac{U}{D}$). The nanometer size crystal is needed to observe vacancy drift. We would expect a breakthrough to occur in material at so high electric field. The fact that we are talking about ionic crystal saves us. Ionic bond is very strong and much higher field is needed for ionization.

3.2.1 Quantum or classical?

To determine the conductivity of doped ionic crystals, it is crucial to decide whether to consider quantum or classical. In the previous chapter i have already mentioned that the ion is too massive for tunneling. We can show this formally. Let us discuss the transition of the particle through the square barrier (figure 4).

![Figure 4: Square potential of length $z_0$ and height $V_0$. $\psi_i$ is wave function of a particle in every region ($i=1,2,3$). The arrows illustrate the particle travels through the barrier.](image-url)
We can write down the whole wave function as followed.

\[ \psi = \begin{cases} 
\psi_1 = a_1 e^{ik_1 z} + b_1 e^{-ik_1 z} & z < 0 \\
\psi_2 = a_2 e^{ik_2 z} + b_2 e^{-ik_2 z} & 0 < z < z_0 \\
\psi_3 = a_3 e^{ik_3 z} & z > z_0 
\end{cases} \]

\( k \) denotes the wave vector that is \( k_1 = k_3 = \frac{1}{\hbar} \sqrt{2mW}, k_2 = \frac{1}{\hbar} \sqrt{2m(W - V_0)} = i\kappa \). \( W \) is particle energy and suits to \( 2e_0 Ec \) in our case. Considering the boundary conditions we easily came to the well-known formula for probability of tunneling.

\[ P = \frac{4k_1^2k_2^2}{k_1^2 + \kappa^2} e^{-2\frac{z_0}{\hbar} \sqrt{2m(V_0 - W)}} \tag{3} \]

As there appears oxygen ion mass in exponent, which is approximately \( 1.5 \times 10^{10} eV/c^2 \), the probability of tunneling is incredibly low. It tells us that the ion in ionic crystal act classical. Let’s see what happens when the particle energy is greater than the barrier height (\( W > V_0 \)). Classically we expect that in this case, the probability of a transition is one. Quantum there is a final probability of a particle to deduct of a barrier. The probability of particle passage across the barrier in the case when its energy is higher than the barrier height, is calculated in the same manner as the probability of tunneling (figure 5).

\[ P = \frac{1}{1 + \frac{1}{4} (\sqrt{\frac{W-V_2}{W}} - \sqrt{\frac{W}{W-V_0}})^2 \sin^2(\frac{z_0}{\hbar} \sqrt{2m(W - V_0)})} \tag{4} \]
\[ W = 2e_0 E c, \ V_0 \] is barrier height and \( z_0 \) is barrier width. Oxygen ion mass appears this time in sine argument in denominator. Huge mass in argument means huge frequency of sine so its wave length is short. Thermal fluctuations energy is much bigger than difference between two sine peaks in probability dependence of energy. This confirms that this ion behaves completely classically. Taking into consideration the previously established fact that the tunneling probability is equal to 0, we obtain the searched dependence of the whole energy spectrum. Probability of ion to pass through the barrier increases from 0 to 1 as soon as the ion energy reaches a barrier height (figure 6).

![Figure 6a](image1.png) ![Figure 6b](image2.png)

Figure 6: Probability dependence of energy. Figure 6a shows plotted probability from equation (4) that is quantum probability of particle crossing the barrier. Figure 6b shows the same dependence as figure 6a with thermal fluctuations taken into account. This is classical limit which is reached in our case of oxygen ion.

We found out, that if the electric field is high enough the vacancies can diffuse inside the doped metal oxide.

### 3.3 Alternative interpretation

The events in electric field, can be interpreted in an alternative way. We can imagine that in an electric field all the ions of the lattice move. Positive ions move in field direction and negative ions in opposite direction. Crystal lattice become distorted. If there is one vacancy in lattice instead of negative ion, it moves in field direction as it is charged positively. Distances between positively charged ions stays unchanged and so the distances between negative ions. Only the distance between vacancy and its nearest negative ion in field direction, changes. This distance is reduced. If the field is so large that the vacancy and the ion find themselves in the same place (the distance
is reduced to zero), this is completely equivalent to the transition described above (figure 7 and 8).

Figure 7: Unit cell of titanium dioxide rutile, distorted by field in z direction. Blue spheres represents the titanium ions, red spheres are oxygen ions. The two oxygen ions from lower surface of unit cell are moved to next unit cell.

Figure 8: The same scheme as the figure 7. Instead one oxygen ion there is vacancy. Vacancy influenced by electric field moves to the same direction as titanium ions and so the distance between it and the nearest oxygen ion reduces. The dashed line links the vacancy and oxygen ion that changes their places if field is strong enough.
4 Doped and undoped crystal junction

Now when we know that vacancies can diffuse inside the electric field we can imagine two regions of metal oxide. If one region is doped and the other is undoped we get some interesting phenomena on their contact if the junction is inside electric field. This junction is actually a memristor[2] (figure 9). Let see how it works.

Figure 9: Schematic configuration of the doped and undoped ionic crystal junction.[1]

If such a junction is exposed to electric field, so that field points from doped to undoped part, vacancies diffuse into an undoped part. Equivalently we can say that ions from undoped part change place and fill the vacancies in doped part. Concentration of vacancies in doped part decreases. In doped part there occur some vacancies near the contact. Undoped part is thus gradually changed in to the doped part. We can imagine as if the border between doped and undoped part moves in field direction. Doped part increases and undoped decreases. It may happens that the vacancies overwhelm the entire undoped part and there left us only doped. Electrical resistance of such an element changes dramatically during this because doped part is conductor and undoped part is good insulator. If we turn the field from undoped to doped part the reverse effect occurs. The volume of undoped part increases and volume of doped decreases. Concentration of vacancies in doped part increases. The resistance of junction in such a case
increases. Border between both parts again moves in to the field direction, but there is one basic difference between border moving into the doped or undoped part. When border moves to the doped direction there is no way for it to reach the edge and the whole element becomes undoped because the number of vacancies is unchangeable. When we turn of the field the vacancies moves no more because they are bonded well. The element stays in the state as it was at the moment we turn of the field. We can say the element "memorize" to what field for and how long it was exposed to. Electric field changes resistance of junction but when we turn of the field the resistivity stays unchanged. Memory characteristics of such contact are obvious. The advantage of such a memory element is passivity and nanoscale size.

4.1 Diffusion

We calculate that at the high electric field, vacancies can diffuse inside the metal oxide. Vacancies diffusion can be described by a diffusion equation.

$$\frac{\partial n(x, t)}{\partial t} = D \left[ \frac{\partial^2 n(x, t)}{\partial x^2} - \frac{E(t)}{k_b T} \frac{\partial n(x, t)}{\partial x} \right]$$

(5)

This is well known diffusion equation with one more term on the left hand of equation, that is contributed by electric force. This equation describes the dynamics of vacancies density \( n \). It can be solved numerically. The results are presented on the figure 10. Initial conditions for this equation are, that we have a thin layer of doped metal oxide on left edge of device. The blue part is undoped region. From the figure we can se that whole region of vacancies is moving to the field direction. The vacancies density is not dramatically changed during this process. Such an event would not dramatically change the resistance of the device.

4.2 Diffusion with vacancies interaction

4.2.1 vacancies interaction

It turns out that we get much better match of this model with the experiment if we take in count the vacancies interaction. Vacancies are charged so they repulse each other because of electrostatic coulomb potential. But that is not the only interaction between two vacancies. Vacancies cause the distortion of the crystal lattice. The energy of the distorted lattice is lower if two vacancies are near each other. This interaction between two vacancies is attractive. Lennard-Jones potential is good approximation for this attractive interaction.
Figure 10: The solutions of the diffusion equation inside the electric field in two dimensions. Initial conditions for the equation are, that we have a thin layer of doped metal oxide on left edge of device. The blue part is undoped region. Colors from blue to red represents the vacancies density. The calculation is made for three different times after the electric field is turn on. The time scale is arbitrary[3]

The expression for height of potential between two vacancies can be written down like sum of Lennard-Jones potential and Coulomb potential[3].

\[
W(r) = A \exp(-r/a) - \frac{B}{r^6} + \frac{q^2}{\pi \varepsilon_0 \varepsilon r}
\]  

(6)

Attractive part of potential is stronger then repulsive. This is the consequence of high charge screening in ionic crystals. The electrostatic repulsion between vacancies is noticeable only on very small distances.

4.2.2 Toy model of memristor with vacancies interaction

If we rewrite diffusion equation so that we take in count vacancies interaction some interesting results are obtained. This equation is again solved numerically with Monte Carlo method. This toy model was made for 75 vacancies inside the memristor. The real number of vacancies is of course much larger but anyway this model tells us surprisingly lot about vacancies dynamics inside the memristor. Figure 11 is the result of this model.
Figure 11: Figure (a) is initial state of the memristor. There is the doped part on the bottom and undoped on top. Red spots marks vacancies. Again we have only thin layer of doped metal oxide on one edge of device in its initial state. Then device is exposed to the short electric pulse. Pulse duration is denoted as $t_p$. The vacancies are immediately after a pulse homogenously distributed around the body of memristor (figure (b)). But this is not the stable state. After the time, five time longer than time of pulse $t_p$, the distribution from figure (c) is obtained. We see that vacancies are arranged in clusters, because the attraction potential we include in to the model. This is the stable distribution. It had not change since the end of simulation no matter how long it ran. Figure (d) is memristor in its state after another electric pulse in reverse direction. As expected, the vacancies diffuse back while exposed to electric pulse and state similar to initial state is obtained. [3]

4.2.3 percolation paths

If we use more precise model with 150 vacancies included, we can try to find out the pattern of clustering. For the periodic boundary conditions and for impenetrable boundaries this model was calculated (figure 12). In both cases the clusters have a shape of long chains called percolation paths. Percolation paths are called so, because they are actually a conductive lines inside the material. The lack of oxygen in the region of cluster is so huge, that
crystal structure is completely changed there. In case of TiO$_2$ we get inside and around this clusters the crystal of Ti$_4$O$_7$. This compound of titanium and oxygen conducts electric current. We actually get a thin channel of conducting phase through the body of device if we expose it to the electric pulse. Device is in the good conducting mode. With another electric pulse in reverse direction, we can put the device back in to the state that is similar to initial state. In this state the device conducts no more. Obviously we have the device, that can be switched with the electric pulse from one to another state. The bipolar switch by definition.[3]

![Figure 12: The percolation paths are noticeable in both cases. In the case of impenetrable boundaries the percolation paths are established near the boundary of device. It was measured that electric current inside the memristor is localized near the boundary. [3]](image)

5 Conclusion

The model I presented in seminar is one of the most promising models of memristor. It explains the conductance of doped metal oxide. But it is not the only existing model. Like all other models this model has some inconsistency with the experiment to and the right mode is still the matter of debate.
References


