Magnetic Tunnel Junctions with Alq_3 as a Barrier

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August 2, 2005

Abstract

The aim of this paper is trial of using unpurified 8-hydroxyquinoline aluminum (Alq_3) as a tunnel barrier in a spin-dependent system, a Magnetic Tunnel Junction (MTJ).

Basic principles os MTJs are discussed and termal deposition, a common technique of creating MTJs, is described. Quality of Alq_3 films deposited on a glass substrate is measured with Cu Kα X-Ray Diffraction, organized structure of the films is shown. Layers of cobalt, aluminum oxide, 8-hydroxyquinoline aluminum and permalloy ($Co/AlOx/Alq_3/PY$) are deposited. TMR has been achieved, up to 5.2% and 8.8% for room and liquid nitrogen temperature, respectively. Spin polarisation of Alq_3/PY interface was observed to be positive.

1 Introduction

1.1 Spinotronics

Progress in the development of magnetic storage devices relies heavily on a rather young branch of solid-state physics — spinotronics. As its name suggests, this discipline involves utilizing the quantum spin of electrons.

A particle's spin is a type of intrinsic angular momentum. For an electron, its value is always $-\frac{1}{2}\hbar$ or $\frac{1}{2}\hbar$. Since the electron is a charged particle, the spin makes a magnetic dipole. Therefore, every single electron is effectively a up-or-down magnet.

In a ferromagnet electrons are the source of magnetization. When a sufficiently large number of electrons' magnetic dipoles point the same direction, the total magnetization points the same way too. Consequently, external magnetic field can magnetize a sample and align spins in a certain way.

1.2 Giant Magnetoresistance

One important phenomenon is that when two ferromagnetic plates are connected together, the total resistance depends on the relative direction of spins in the plates. When both ferromagnets are magnetized in the same direction, spins of electrons are parallel and the structure has electric resistance R_P. In the case of opposite magnetization, spins are anti-parallel, and the resistance is R_{AP}. It is observed that $R_P < R_{AP}$, an effect known as the Giant Magnetoresistance (GMR). The simplest explanation for this is that the scattering amplitude is greater for electrons traveling to a place with different spin polarization.

1.3 Tunneling

In classical physics, when two conductors are separated by an insulator and the potential energy in the insulator is higher than energies of electrons, there is no possibility fo the electrons to pass through so-called forbidden area. Therefore, no current can flow between them. However, quantum mechanics gives electrons a finite probability to jump over, or tunnel through an insulator. This chance depends exponentially on both energy barrier height and its thickness.

Since the barrier level is fixed (usually with energy below $10\,eV$), the only thing one can manipulate is the thickness. For most cases an order of magnitude of $10\,\mathring{A}$ allows an observable amount of electrons to tunnel through. Two metals separated by an insulator through which current can flow, are called a Tunnel Junction (TJs).

1.4 Magnetic Tunnel Junctions

One can think about phenomena related to both tunneling and spin properties. Indeed, when an electron tunnels, its spin is conserved which creates possibilities for further applications. In general, Tunnel Junctions with dependence on magnetic field are called Magnetic Tunnel Junctions (MTJs).

To achieve so-called spin polarized tunneling, a spin source, an insulator, and a spin detector should be used. The simplest idea is to use two ferromagnets with the insulator between them. This 3-layer setup can be written as Ferromagnet 1 / Insulator / Ferromagnet 2 system (or FM1/I/FM2).

When both ferromagnets are magnetized, each one favors one spin to another. Also resistance difference is observed. Hence, we can define the TMR parameter - a good indicator of a MTJ quality:

$$TMR \equiv \frac{R_{AP} - R_P}{R_P}.$$

There had been little interest in the topic until 1995, when it was shown by Moodera et al. that even at room temperature it is possible to obtain magnetoresistance in a MTJ with TMR value 11.8% [1]. Cobalt-iron alloy and cobalt were used as the ferromagnets and aluminum oxide as the barrier (CoFe/Al_2O_3/Co).

1.5 Objectives

Although various materials can act as a barrier in MTJs, most studies use inorganic materials, especially metal oxides.

Very recently, Xiong et al. has shown that an organic molecule, 8-hydroxyquinoline aluminum (Alq_3) can be applied as a tunnel barrier [4]. Furthermore, they have measured a spin polarized tunneling to a certain degree. However, the emphasis was put on lower temperatures (mainly $11\,K$) and the TMR was relatively low ($< 1\%$ at room temperature). Additionally, the mentioned thickness of the barrier seems to be surprisingly large.

The aim of the research described in this paper is to improve results on MTJ with 8-hydroxyquinoline aluminum ($Alq_3$3) as a barrier, with goal of increasing TMR, especially at room temperature.

2 Alq_3

This section introduces applications and physical properties of 8-hydroxyquinoline aluminum (Alq_3), the material that has been used as a barrier.

The bright history of Alq_3 started in the year 1987 when high-efficiency Alq_3-based Organic Light-Emitting Diodes (OLEDs) were reported. Since then numerous researches have been carried out to optimize quality of OLEDs containing this compound, as well as to understand its physical properties [5].

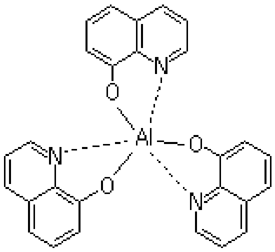

Figure 1: Alq_3, $C_{27}H_{18}AlN_3O_3$, 459.44 g/mol.

Usually, Alq_3 is a yellowish-green polycrystalline powder with strong photoluminescence. it contains mainly α-phase, with meridional isomer [6]. This compound has energy gap $2.8\,eV$, what makes it a semiconductor. As an organic material, its band structure is much less sensitive that inorganic ones.

3 Preparation of a MTJ

To create a Magnetic Tunnel Junction one have to layer films of various substances on a substrate. For the range of thickness appropriate for MTJs the possible techniques involve evaporating a source substance and then sticking its vapor to a previous layer. In order to avoid contaminations, at least high-vacuum[1] has to be used as the environment of the process.

3.1 Vacuum chamber

High-quality glass (SiO_2) substrates are cleaned in an isopropanol vapor bath. Both substrates and source materials are put in a vacuum chamber. Alq_3, because of its low sub-

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[1] high-vacuum - a volume with pressure in range of $10^{-3} - 10^{-8} torr$ ($\approx 10^{-1} - 10^{-6} Pa$)

limation temperature (about $210°C$) is placed in a crucible pot surrounded by a tungsten heating wire. Materials with a higher evaporation temperature are placed as a target for an electron gun. The air is pumped out by a mechanical roughing pump and a diffusion pump to a pressure of about $10^{-7}\,torr$.

Most substances entrap gas in their cavities. Therefore, it is crucial to remove it to maintain the aimed purity. Gas capacity varies greatly with temperature — higher temperatures decrease capacity dramatically. Consequently, the gasses trapped in materials in the chamber can be removed by heating. Since the released gas is now in the vacuum chamber, a temporary increase of the pressure is observed. To continue one have to wait until the pump system expels this gas, so the pressure reaches the previous level.

To protect the substrate from an uncontrolled deposition, it is covered by a shutter (an ordinary metal plate that can be moved away). Also, each deposition only a particular part of the substrate should be deposited. The simplest and most convenient way is to use a few masks — pieces of metal with a hollow pattern inside. For MTJ purposes, there are two masks - – one with a single long strip and one with 6 strips perpendicular to the other mask (Figure 2).

Figure 2: Two different masks needed to create MTJs.

To deposit a layer, the source is heated either by the heating wire or the electron gun. The speed of deposition is measured by a Quartz Crystal Monitor with a sufficiently good precision (order of $0.1\mathring{A}/s$). When it approaches the aimed level, the shutter is manually turned on and the real deposition starts. Thickness is measured also by the same Quartz Crystal Monitor. When it reaches the desired value, the shutter and heater are turned off.

4 Taking measurements on a MTJ

Roughly speaking, every measurement involves investigating the dependence the current flowing through the MTJ (I) on the bias voltage (V), the applied magnetic field (H) and the temperature in which the MTJ works (T). In ordinary cases, 2 independent parameters are fixed and only one is varied [2].

4.1 4-point probe

The essential thing in measurements of voltage is to be sure that it is voltage only on the probed sample. To eliminate observing voltages on wires and contacts a 4-point probe may be carried out (Figure 3).

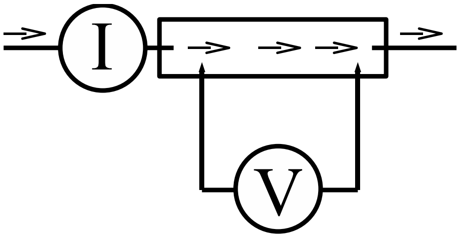

Figure 3: Two different masks needed to create MTJs

In this case voltage components on other parts than the probed one can be neglected. Thanks to its simplicity, this method is widely used in measurements of resistance. If it is not said otherwise, resistances are measured by the 4-point probe method.

4.2 $I(V)$ characteristics

Perhaps the most basic measurement for a high variety of electronic elements is its current-voltage characteristics. For ordinary resistors, Ohm's law is satisfied (R - resistance, a constant)

$$I(V) = \frac{1}{R}V$$

so the function is linear.

For Tunnel Junctions the $I(V)$ relation can be still written in a similar way, taking into account R is no longer a constant (it decreases slightly with voltage).

Often, it is good to approximate the TJ $V(I)$ function as third-degree polynomial with no constant component (Taylor series expansion, with no voltage there is no current).

$$I(V) = aV + bV^2 + cV^3 \tag{1}$$

When a, b, c factors as well as the TJ area are known, barrier thickness and energy can be calculated from the Brinkman's $I(V)$ equation.

$$I(V) = SG_0 \left(V - \frac{A_0 \Delta\varphi e^2}{32\varphi^{3/2}} V^2 + \frac{3A_0^2 e^3}{128\varphi} V^3 \right) \tag{2}$$

$$G_0 = \frac{e^2\sqrt{2m}}{(2\pi)^2\hbar^2} \frac{\sqrt{\varphi}}{d} \exp(-\frac{2d}{\hbar}\sqrt{2m\varphi}),\ A_0 = \frac{4d}{3\hbar}\sqrt{2m}.$$

Note that when the junction is symmetric, $b = 0$.

The same equation applies to MTJ. Therefore properties of the Alq_3 barrier can be discovered by fitting Equation (2) to the measured $I(V)$ curve.

4.3 Magnetoresistance

The most important measurement for MTJs is magnetoresistance hysteresis. It determines the efficiency of spin polarized tunneling with the TMR parameter.

4.3.1 Hysteresis loop of a ferromagnet

Before discussing magnetoresistance, basic information about ferromagnetism should be reviewed. In general, for every material there is a dependence of magnetization (M) on the external magnetic field (H). Ferromagnets are unique in that the dependance creates a loop in $M(H)$ plane. It means that M does not only rely on the current value of H but also on the previous magnetization. Consequently, ferromagnetism brings about some kind of 'inertia'.

Strong ferromagnets tend to be magnetized almost all the time with maximum value (magnetization saturation, M_s). It is possible to change change the magnetization by applying $H > H_c$ (H_c - coercivity field).

4.3.2 Two ferromagnets and sweeping

When the two ferromagnet electrodes (FM1 and FM2) are made of different materials, they do not respond to the external magnetic field in the same way. Namely, they may have different coercivity fields ($H_{c1} < H_{c2}$). When starting from a sufficiently large negative field $H < -H_{c2} < -H_{c1}$, both FM have $-M_s$ magnetization. When H sweeps from its starting value to positive values, magnetization remains the unchanged as long as $H < H_{c1}$. When this point is reached, FM1's magnetization changes the sign. Then when $H_{c1} < H < H_{c2}$, FM1 and FM2 are magnetized in the opposite (anti-parallel) directions. Later, after passing H_{c2}, both FM layers are again magnetized in the same (parallel) way. Now they have $+M_s$.

4.3.3 Magnetoresistance

At a fixed voltage and a fixed temperature magnetic field sweeps from a chosen negative value the same value with positive sign and then backwards (e.g. from $-100\,Oe$ to $100\,Oe$ and then to $-100\,Oe$). All the time resistance (V/I) is measured.

Combining informations from sections 1.4 and 4.3.2 brings an interesting result. During the sweep the resistance varies in a very specific way. It remains constant (R_P) to one point, then it rises quickly to achieve R_{AP}, holds this value for a moment, falls to R_P.

In this case R_P and R_{AP} are simply found as the smallest and the largest resistances on the MR curve, respectively. Hence, TMR(T,V) can be determined.

5 Results and discussion

5.1 Film quality

The first essential thing to measure is the crystal structure of the grown film. Three different samples have been made, in similar conditions but different deposition rate (Table 1).

Sample No.	Thickness	Pressure	Deposition rate	Peak position 2θ
1	$1.0\,k\mathring{A}$	$4.2 - 4.8 \times 10^{-7}\,torr$	$6.0 - 6.9\,\mathring{A}/s$	29.3°
2	$1.0\,k\mathring{A}$	$4.4 - 5.2 \times 10^{-7}\,torr$	$1.3 - 1.7\,\mathring{A}/s$	29.4°
3	$1.0\,k\mathring{A}$	$5.0 \times 10^{-7}\,torr$	$0.8\,\mathring{A}/s$	29.3°

Table 1: Data for $1.0\,k\mathring{A}$-thickness Alq_3 films deposited at room temperature on SiO_2 substrate. Position of the only significant Cu Kα X-Ray diffraction peak is given.

Cu Kα (wavelength $1.54\mathring{A}$) X-Ray Diffraction [7] has been performed to gather informations about the crystal structure. In all of the samples, only one 2θ peak has been detected (Figure 4). It implies that only one angle satisfies the Bragg condition and therefore only one crystalline structure has been deposited. The result is markedly different for polycrystalline powders in which numerous peaks are observed [5].

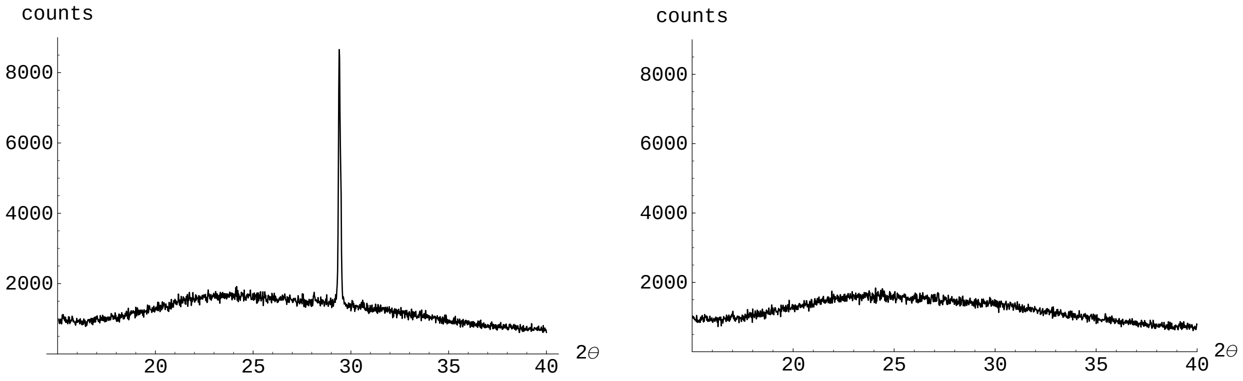

Figure 4: X-Ray Diffraction spectrum for glass substrate with (left) and without (right) Alq_3 film. Sample No. 3.

Hence, one can suspect that quasi-epitaxy has been achieved [3]. Nevertheless, Alq_3 in barriers have thickness at least one order of magnitude lower than the film described above. Hence, it is a risky assumption to think that a thin Alq_3 film has only one crystal structure.

5.2 Thickness and resistance

Multilayered samples were grown on SiO_2 substrate at room temperature, under pressure of $5 \times 10^{-7} torr$.

There where deposited films of silicon monoxide ($10\,\AA$), cobalt ($80\,\AA$), aluminum ($5\,\AA$) oxidized by plasma, 8-hydroxyquinoline aluminum (various, $29-255\,\AA$), permalloy [2] ($100\,\AA$) and a protective layer of Aluminum ($10\,\AA$). Excluding the seeding and the protective layer, one can abbreviate it by Co/AlOx/Alq_3/PY.

The main issue is that the resistance of MTJ is extremely sensitive to the thickness of the barrier. Too thick of a barrier keeps resistance out of the measuring devices' range, whereas too thin may lead to a short. In practical experience, only MTJs with resistance between $50\,k\Omega$ and $2\,M\Omega$ are useful for further investigations. Others are either shorted or far too resistive (relatively small current going through them cannot be measured accurately).

The vacuum system provided little control over the deposition speed, so the exact thickness is unknown. Furthermore, even MTJs from the same batch may differ, mainly due to uneven deposition. A significant amount of following measurement have been performed on one junction, with $58\,\AA$ of Alq_3.

5.3 $V(I)$ Characteristics

Voltage-current characteristics is particularly easy to measure. As long as resistance of a MTJ is not greater than $2\,M\Omega$, the noise is sufficiently low. To observe a sufficiently good third-degree curve, one need to fix the sweeped voltage range to be as broad as possible. However, it is necessary to avoid destroying the junction. Voltage near and above $500mV$

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[2] Permalloy — An alloy of 80% Fe and 20% Ni

is claimed to be dangerous for a MTJ. Therefore, measurements uses voltage below $300mV$; behaviour at room and liquid nitrogen temperatures is investigated (Figure 5).

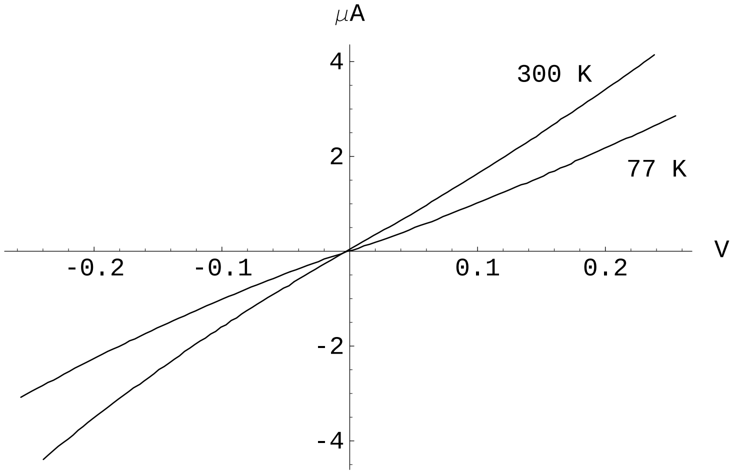

Figure 5: Typical $V(I)$ curves for $77\,K$ and $300\,K$. At lower temperature resistance tends to be higher.

One can then calculate barrier energy from Equation (2). For these junctions average energy φ varies from 1.5 to $2.0\,eV$. It is hard to say, if the divergence has its origin in different barriers or rather noises. Due to existence of aluminum oxide, the whole barrier is asymmetric. In the taken approximation, the barrier energy changes lineary. However, there is a relatively large inconsistency between the computed energy differences. The results are in the range from -0.6 to $1.9eV$.

5.4 TMR

TMR was measured for two temperatures - of room and of liquid nitrogen. The hysteresis was clearly observed for both of them (Figure 6). What should focus attention, its shape changes with temperature too. To investigate this problem, one need to know response of Co and PY to temperature changes.

Dependance of TMR on the bias voltage was investigated (Figure 7). It brought TMR

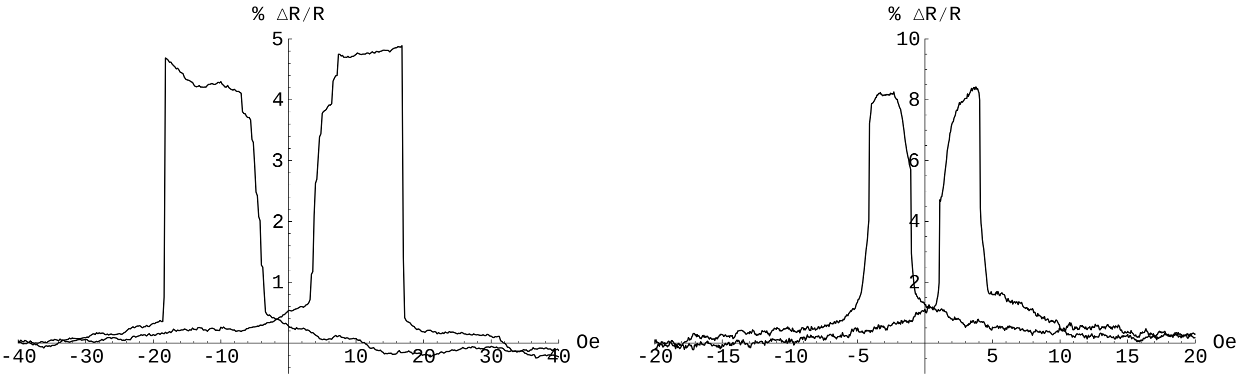

Figure 6: TMR loops: $25\,mV$ at $300\,K$ (left), $-5m\,V$ at $77\,K$ (right)

of 5.2% and 8.8% for room and liquid nitrogen temperatures, respectively.

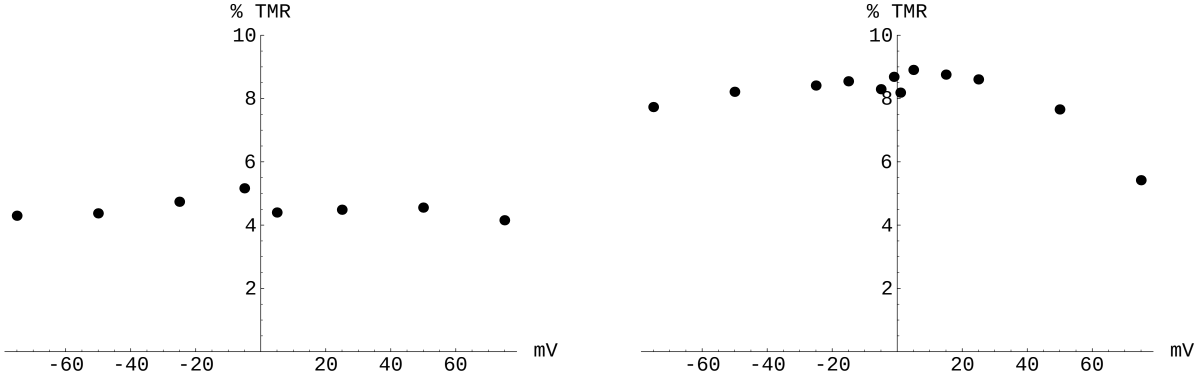

Figure 7: TMR with dependance of the bias voltage. $300\,K$ (left) and $77\,K$ (right)

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One can clearly see asymmetry between positive and negative voltage (Figure 7). At this point it is important to add that positive voltage means that cobalt is the cathode (charged positively) and permalloy is the anode. Although, it is not clear if spin polarised tunneling is affected, or any tunneling at all.

5.5 Sign of polarisation

The actual spin of tunneled electrons relies on alignment electrons on the interface. I some cases they behave in a normal way - staying along the magnetization (it is called positive polarisation), but in some materials, they face the opposite direction (negative polarisation).

Since it is known the polarisation on Co/AlOx interface is positive [1] and it is measured that Co/AlOx/Alq$_3$/PY Magnetic Tunnel Junction has the lowest resistance when magnetization is parallel, Alq$_3$/PY polarisation should be positive too. Obviously, it refers only to the range of voltage that was measured.

6 Conclusion

The goal of the project was satisfied to some point. Quality of deposition of unpurified 8-hydroxyquinoline aluminum (Alq$_3$) was measured, with result suggesting a layer-organized structure. Working Magnetic Tunnel Junctions with Alq$_3$ as a barrier were made. TMR has been achieved, up to 5.2% and 8.8% for room and liquid nitrogen temperature, respectively. Spin polarisation of Alq$_3$/PY interface was observed to be positive.

However, there is still much room for further researches. TMR may be still optimized, and efficiency of direction-dependent flow of current - increased. Dependence of electroluminescence with spin polarized tunneling may be tested.

7 Acknowledgments

I would like to thank Dr. Jagadeesh Moodera, my mentor, for all the time, care, kindness, knowledge and useful advises he gave to me. Also I would like to thank Patrick LeClair for fruitful discussions and help in experiments, Tiffany Santos for the preparation of samples, John Philip for X-Ray measurements, as well as other laboratory workers.

My deepest gratitude to all those who helped me with adding, editing and putting this into LaTeX as well as those who corrected my poor grammar (Vivek, Dennis, Jenny).

I would like to thank those people, who gave me possibility to participate in RSI'05, with emphasis on Dr. Ryszard Rakowski, the secretary of the Polish Children's Fund.

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