Idaho Incubation Fund Program

Progress Report Form

Proposal No.	**IF 14 004**
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Name of Institution:	**Boise State University**
Project Title:	**Research on Films with Columnar Structure to Improve Memristors Speed, Reliability and Lifespan**
	January 1 – May 31, 2014

Information to be reported in your progress report is as follows (attach additional information as needed):

1. Summary of project accomplishments for the period just completed and plans for the coming reporting period:

Work has been carried out on characterization of the different compositions of the obliquely deposited chalcogenide glass films under different angles with the aid of Scanning Electron Microscopy (SEM), Atomic Force Microscopy (AFM), Energy Dispersive Spectroscopy (EDS) and Raman Spectroscopy as presented in previous report. Each of these respective results provided a partial view of the mechanisms that contribute to a reliable device performance.

In this report, the kinetics of silver diffusion and electrical performance of the Redox Conductive Bridge Memory (RCBM) devices having columnar structure with the chalcogenide films are presented.

Silver Diffusion Kinetics

Since the formation of a solid electrolyte, achieved through photo-diffusion, plays an important role in the device performance, it is imperative to study the silver photo-diffusion dynamics. In this work, the kinetics of Ag diffusion in Ge_xS_{1-x} (x=0.2, 0.4), which are the two limiting cases – the Se richest and Ge richest among the studied films are studied by Neutron Reflectometry.

Two types of measurements were performed in this work: static and transient. The Fourier Transform of static neutron reflectivity profiles for both the samples, before and after the light illumination is presented in Figure 1. The peaks in Figure1a, correspond to 400Å (Ag), 1200Å (a-$Ge_{40}S_{60}$) and 1600Å (total thickness), which confirms a two layer structure. After illuminating the sample with visible light, the reflectivity profile has changed, indicating some degree of silver diffusion into the $Ge_{40}S_{60}$ film. However, the Fourier spectrum indicates that the two layer structure is preserved. Considering the $Ge_{20}Se_{80}$ films, the result presented in Figure1b shows a peak around 100Å that corresponds to the reaction layer. After light illumination, only one sharp peak around 1500Å is observed in Figure1b, which supports the conclusion that the film is composed of one layer.

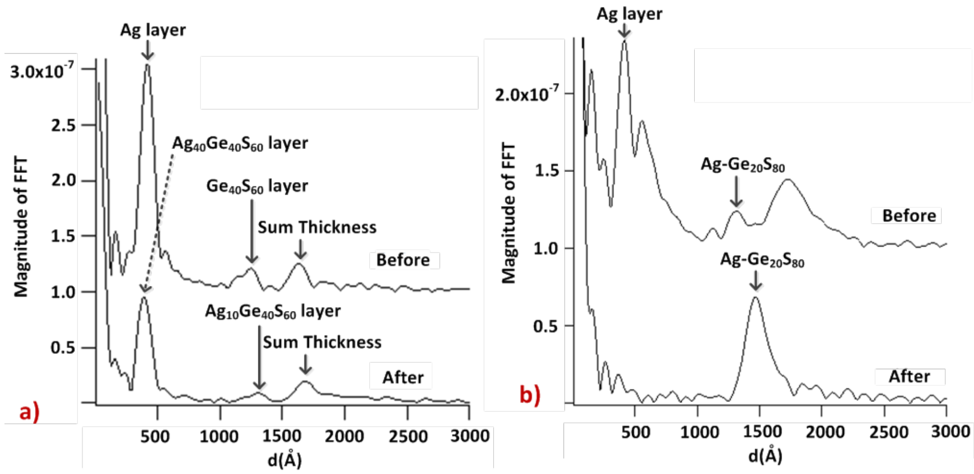

Figure 1 Fourier Transform of the reflectivity data (a) Ag/$Ge_{40}S_{60}$ (b) Ag/$Ge_{20}S_{80}$ films

The Fourier Transform of transient neutron reflectivity data are presented in Figure 2 for both studied compositions with rapid change also being observed to occur in $Ge_{20}S_{80}$.

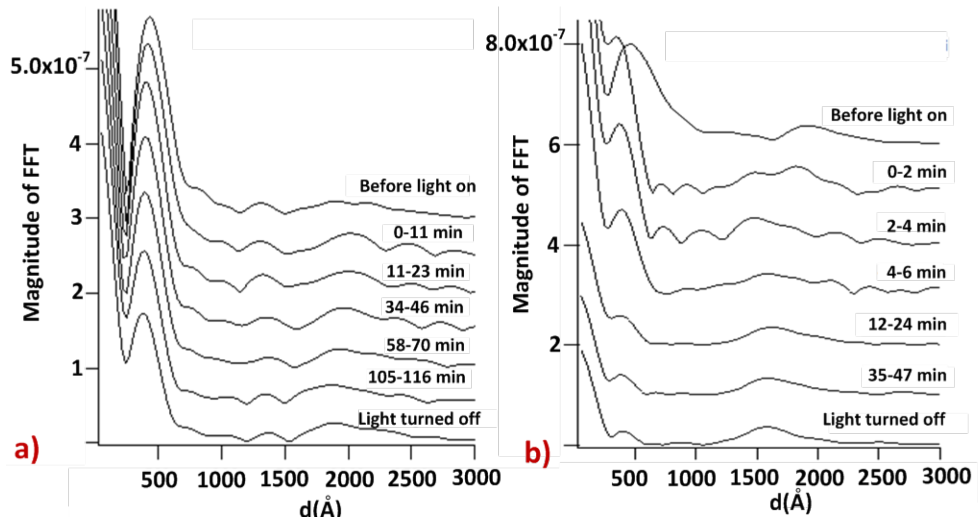

Figure 2 Fourier Transform of the time evolutionary reflectivity data of (a) Ag/$Ge_{40}S_{60}$ (b) Ag/$Ge_{20}S_{80}$

The position and height of the first peak are plotted as a function of time in Figure 3. Two types of diffusion processes are observed, a fast change observed in the first 10 minutes after the exposure starts while a second, slow change is observed after 107 minutes. Even after stopping the light illumination, the change seems to continue. Similarly, in Figure3b the peak position of the first and second peak, and height of the first peak is plotted as a function of time. Again, two diffusion processes can be distinguished: a fast change occurring after 2 minutes since the start the illumination, while a slower change is observed after 20 minutes. The silver diffusion has essentially finished after 20 minutes and the sample becomes a uniform homogeneous layer.

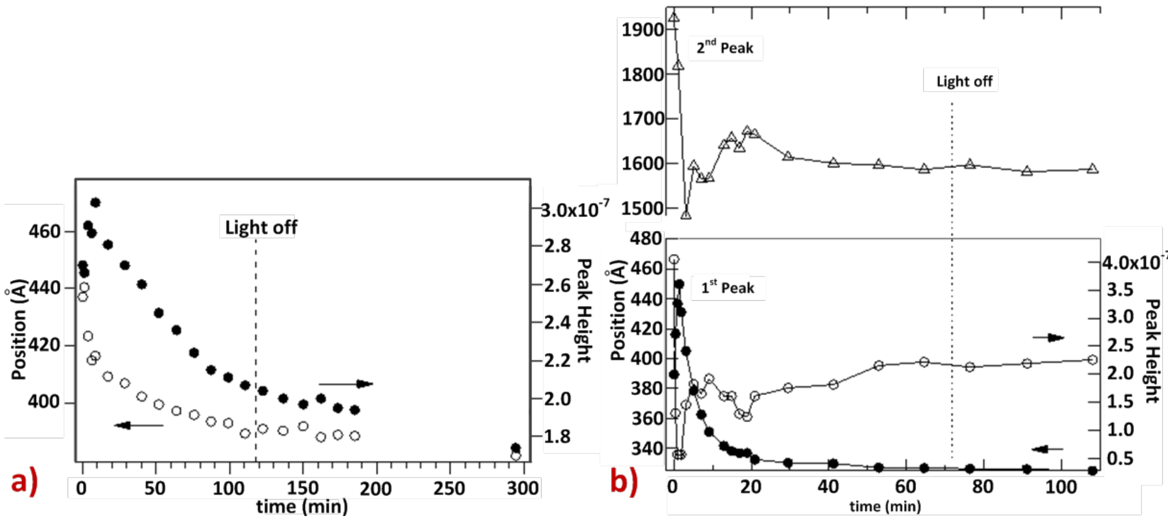

Figure 3 Fourier Transform of the time variation plots: (a) the position (○) and the height (●) of the first peak in $Ag/Ge_{40}S_{60}$ film (b) the positions of the first (○) and the second peaks (△) and the height of the first peak (●) in $Ag/Ge_{20}S_{80}$ film

A difference in the reaction rate is observed in both the systems. The reaction rate in $Ag/Ge_{20}S_{80}$ film is faster than in $Ag/Ge_{40}S_{60}$ film. This compositional dependence is consistent with the structural flexibility of the Ge-S system, which is often explained by a floppy-rigid transition mode. The faster reaction rate in $Ag/Ge_{20}S_{80}$ is attributed to the structural flexibility of $Ge_{20}S_{80}$. However, two silver diffusion processes, a faster and a slower one, are observed in both systems. The two diffusion processes imply the presence of a comparatively stable (metastable) state in the Ag-doped Ge_xS_{1-x} layer. In the first stage, a Ag-rich reaction layer is formed and the Ag layer is exhausted. Considering that the two layer structure is preserved and that the position of the interface is fixed by the completion of the diffusion, the next silver diffusion step takes place from the Ag-rich reaction layer to the Ag-poor reaction layer by getting over the potential barrier between the two layers.

These data have been used to accomplish saturation with Ag of the produced devices which have been further electrically characterized.

Electrical Characterization of RCBM Devices

The RCBM devices were fabricated at Idaho Microfabrication Laboratory at Boise State University. Several electrical characterizations were performed on the fabricated devices as illustrated in the following section:

a) Endurance Measurements

The emerging resistive memories are targeting Flash applications, which require these devices to have an endurance of well over 10^4 switching cycles. The endurance measurements, for the fabricated RCBM devices, were carried out with Agilent 4155B Semiconductor Parameter Analyzer equipped with triax cables to avoid residual charge buildup. The volt-ampere characteristics of the devices with $Ge_{30}Se_{70}$ films deposited normally ($\alpha = 90^\circ$) and obliquely ($\alpha = 45^\circ$ and 60°) are presented in Figure 4. The improvement in the device switching voltage variation is obvious for the devices having columnar structures.

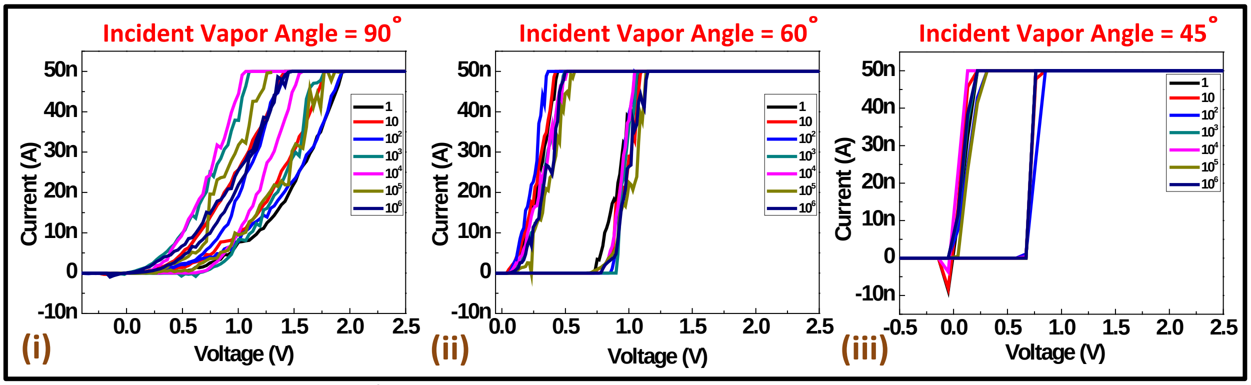

Figure 4 IV curves for 10^6 cycles for $Ge_{30}Se_{70}$ devices having nano-columnar structure in the active films that are deposited under various incident angles: (i) α = 90°, (ii) α = 60°, (iii) α = 45°

Another improvement achieved with the nano-structured devices is the shift of programming threshold voltage to relatively higher voltages. Hence, the probability of devices', embedded into the integrated circuit, falsely switching during an event of noise generation will be minimal. The higher switching voltage is attributed to the reduction of the effective area taking part in the redox reaction. To accumulate the charge Q_o, the ion current $(I = jA_{eff})$, has to be effective for a certain programming time, $t_{prog.}$ This relation can be expressed as:

$$t_{prog} = \frac{Q_o}{j\ A_{eff}}$$

Since with the formation of columnar structures in the devices active layer, the effective area, A_{eff}, participating in the silver ions generation is reduced, thus the time to program (write) the RCBM devices increase, resulting in higher SET voltage of the device.

b) Memory Window

Memory window, for RCBM devices, can be defined as the resistance difference between the ON and OFF states of the device. Mathematically, it can be expressed as:

$$Memory\ Window = R_{OFF} - R_{ON}$$

Having a good memory window will ensure a larger tolerance value for the read out bit stored in the RCBM cell, thus reducing the circuit complexity of the error correction bit.
In the column structured devices, no deterioration has been observed in the memory window. The fabricated devices show four to five orders of magnitude difference between the HRS and LRS as illustrated in the resistance-voltage (RV) plot in Figure 5. The consistency in the switching voltage for devices with columnar structure compared to those with a random structure is also presented on the plot to highlight the improvement achieved in the devices by formation of such nano-structures.

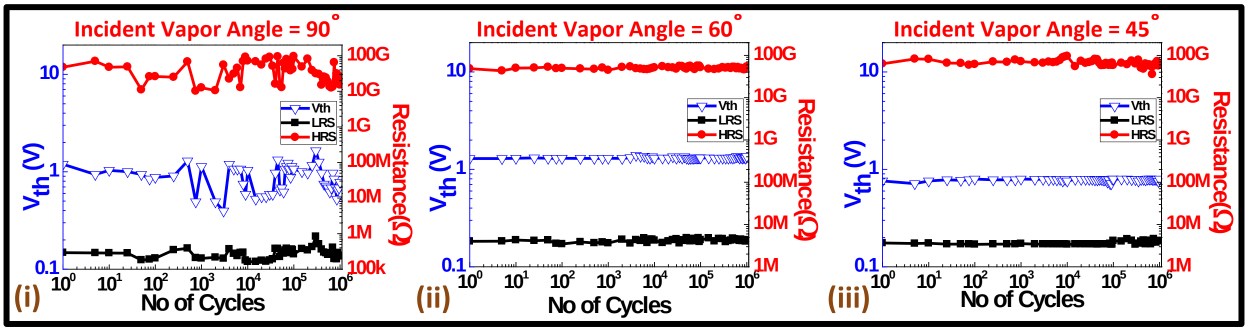

Figure 5 RV plot for 10^6 cycles for $Ge_{30}Se_{70}$ devices having nano-columnar structure in the active films under various incident angles: (i) α = 90°, (ii) α = 60°, (iii) α = 45°

c) Higher Temperature Measurements

In addition to the reliable device performance, the operating temperature range specified for existing memory technologies were investigated for the devices to be commercially viable. The fabricated RCBM devices were tested at 130°C which is well above the required specifications (95°C) of the developed memory technologies. The devices' memory window did not show any degradation in performance as illustrated in Figure 6. However, a slight change is observed in the switching threshold voltage at higher temperature compared to room temperature, which is attributed to thermal activation of the electrochemical process for filament formation.

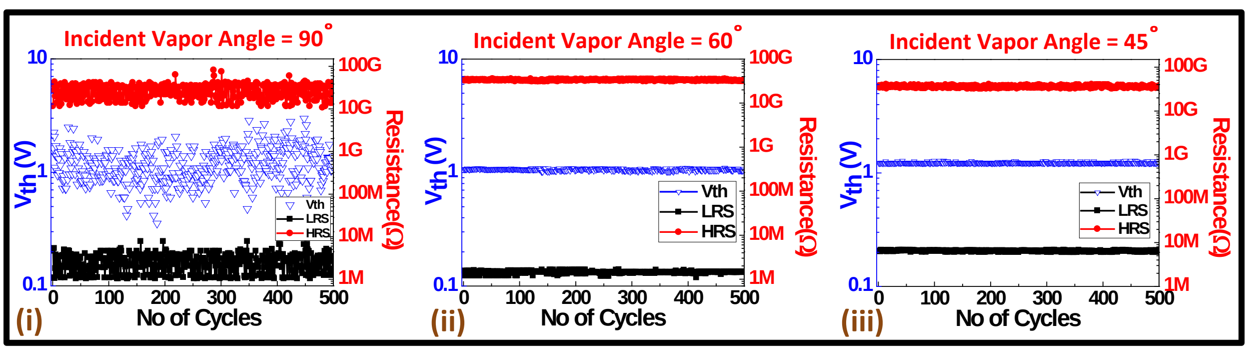

Figure 6 500 cycles of RV plots for $Ge_{30}Se_{70}$ devices having nano-columnar structure in the active films under various incident angles: (i) α = 90°, (ii) α = 60°, (iii) α = 45°

Close observation of the high resistive state reveals a slight decrease in the state, which is in accordance with the expected behavior, i.e. increasing the temperature multiplies the number of charge carriers in a p-type semiconductor, thus enhancing the Ge-Se conductivity and therefore reducing the corresponding resistance. Despite of this reduction in the high resistive value, still more than four orders of magnitude difference is observed in the ON and OFF state of the devices. Hence, no additional temperature sensing circuitry is required to reduce the read out error.

d) Retention Testing

The stability of the memory states of the fabricated column structured devices were analyzed through retention measurements. Once the devices were programmed, the change in state of the device would occur only when the conductive filament deteriorates over time. The fabricated devices were tested for retention properties at 90°C and 130°C to predict the device's lifetime. The state of the programmed devices was detected by reading the state of the cell with the parameter analyzer at specific times with a read voltage ranging from 0.3V to 0.5V. The retention testing results for $Ge_{30}Se_{70}$ devices having nano-columnar structure are presented in Figure 7.

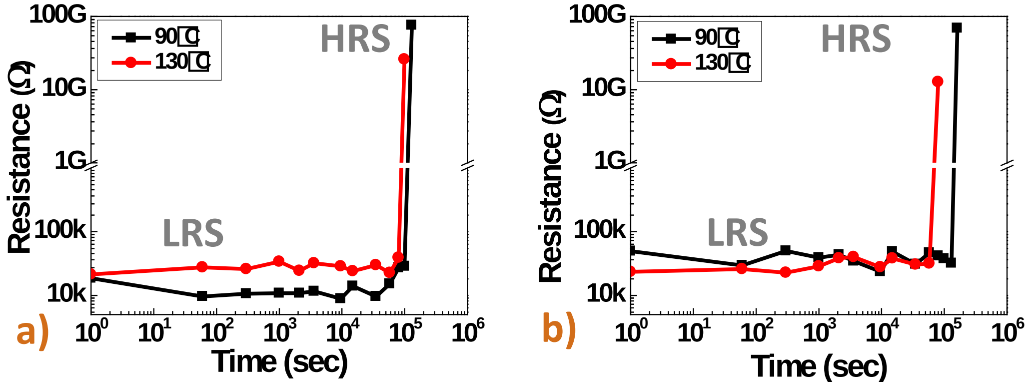

Figure 7 Data retention of low resistive state of the devices written at a compliance current value of 10µA for $Ge_{30}Se_{70}$ devices with (a) α = 60° and (b) α = 45°

The accelerated tested devices for retention properties can be interpolated with Arrhenius theory to predict the actual lifetime of the devices. The stable states achieved with the test results interpolates to over 11 years of data retention. Thus, the devices having the nano-columnar structure are well placed for being used in non-volatile memory applications.

e) Multilevel Switching Capability

A memory cell that can be programmed to more than one state can store multiple bits, which will increase the storage density of the memory architecture. In RCBM technology, the ON state resistance (LRS) of the device can be programmed to multiple resistance levels. This can be achieved by controlling the write current (compliance current) through the cell being programmed. To achieve multilevel switching in the fabricated nano-columnar structured devices, the RCBM cells were programmed with different write current levels controlled by the HP parametric analyzer as shown in Figure 8.

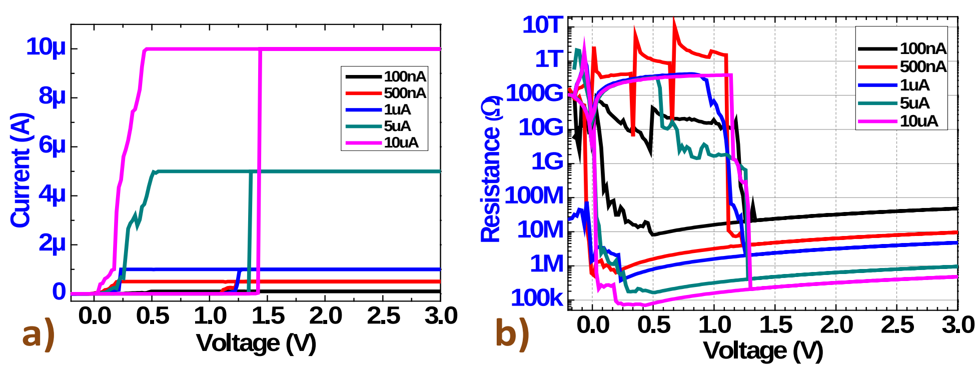

Figure 8 (a) Current-Voltage and (b) Resistance-Voltage curves with varying compliance current values for $Ge_{30}Se_{70}$ column-structured devices with deposition angle, α = 60°

The measured relation between the compliance current and the respective low resistant values is illustrated in Figure 9. A decrease in the low resistance value with increasing the compliance current can be observed. A change in the low resistance value from 5M to 500K is achievable by varying the compliance current from 100nA to 10μm. The presented data illustrate that the low resistance state of the RCBM cell can be programmed to different states by employing a defined compliance current level. This is the key advantage of resistive memory for competitiveness in the emerging memory technology.

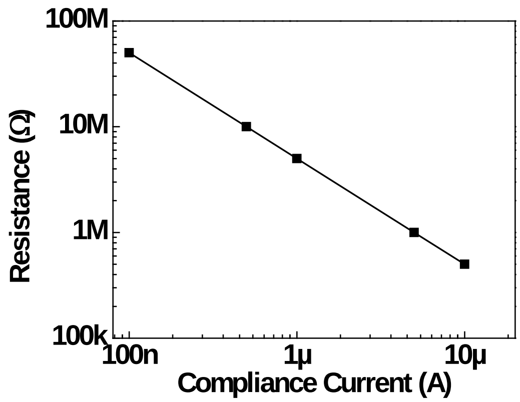

Figure 9 Dependence of low resistive state on the compliance current value at room temperature

Future Plans

We are planning on engineering an experiment to support the hypothesis that the silver filament grows through the columnar structure with no branching within the filament. Since conventional AFM conductivity mapping is based on a contact mode that involves lateral forces leading to sample damage and tip contamination, this may result in artifacts that may disguise the desired information.

To overcome these concerns, AFM will be used in two special modes: Peak Force Tunneling AFM (PF-TUNA) and Peak Force Kelvin Probe AFM (PF-KPFM). Both of these methods will provide insight into the filament growth through the column structure by analyzing the nano-scaled electrical characterization of the fabricated devices. PF-TUNA will be used to record the Ag dendrites growth through the columnar structure while PF-KPFM will enable imaging of the surface potential of the topological layers allowing the flexibility to see Ag distribution within the columnar structure. These nano-electrical characterization techniques will provide near atomic scale information on the fabricated devices, suggesting that these devices are scalable to atomic level.

2. Summary of budget expenditures for the period just completed (include project burn rate):

So far $18,872 are spent in this period of study
The projected burning rate is as follows:

1. Salaries – students (one graduate and three undergraduates), PI and tuition compensation for the graduate student: - 21,570
2. Fringe benefits: - 2,404
3. Payment to rechargeable centers: (IML and BSCMC) – 2,150

4. Travel – 1,898

The real burning rate is very close to the projected one.

3. **Numbers of faculty and student participation resulting from the funding, including internships:** Maria Mitkova- faculty, Muhammad Rizwan Latif PhD student, and four undergraduate students - Tyler Nichol, Brian Dambi, Corey Effew and Jasen Nielsen.

4. **List patents, copyrights, plant variety protection certificates received or pending:**

1) Structured Chalcogenide Glass Films for Redox Conductive Bridge Nonvolatile Memristors (BSU FIle #132, patent app. 61/823,783)

2) Structured Oxide Films for Redox Conductive Bridge Nonvolatile Memristors, (BSU File # 141, patent app. 61/847,974)

5. **List technology licenses signed and start-up businesses created: NA**

6. **Status of private/industry partnerships (include enough information to judge level of engagement):** Micron Technologies (Boise iD) and Adesto Technology (Sunny Vale CA) have been contacted and information about the patent applications and some details about technology have been submitted to them. Right now they are regarding these data, which in essence, are of great interest for them, since work on formation of RCBM devices has been performed by these companies and the presented project offers improvement of the devices technology.

7. **Any other pertinent information that will indicate to the council that the project is meeting satisfactory progress. NA**