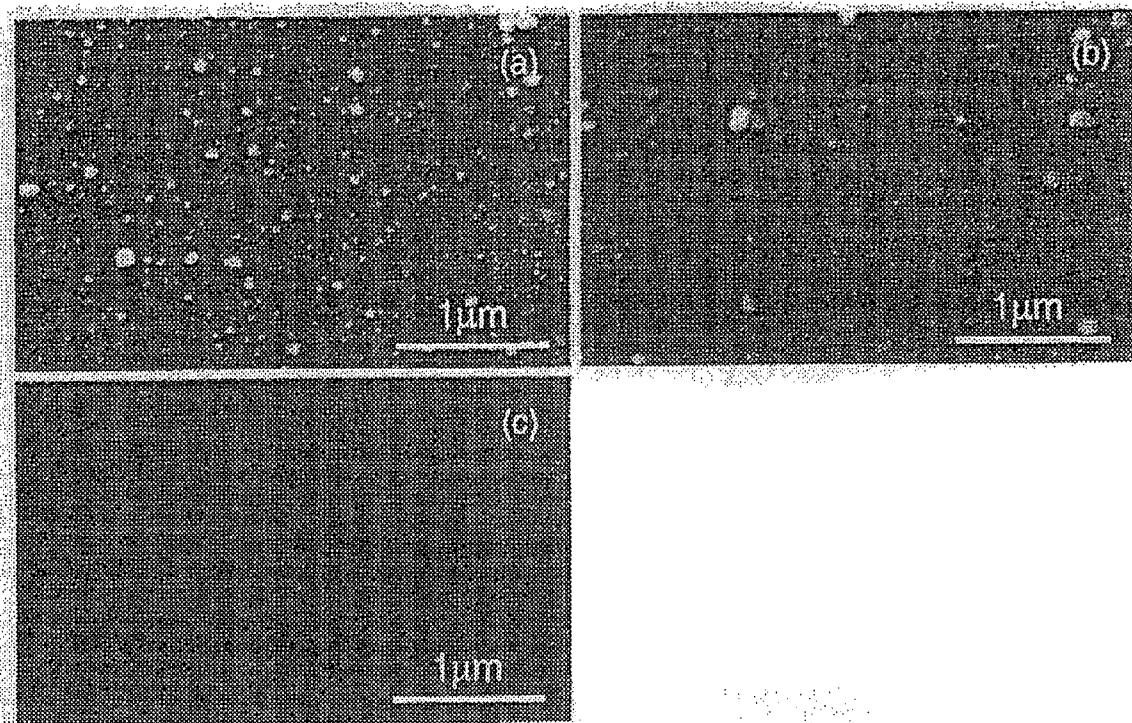




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**Li et al.**(10) **Pub. No.: US 2008/0210921 A1**(43) **Pub. Date: Sep. 4, 2008**(54) **SILVER SELENIDE FILM STOICHIOMETRY  
AND MORPHOLOGY CONTROL IN  
SPUTTER DEPOSITION****Publication Classification**(51) **Int. Cl.**  
**H01L 47/00** (2006.01)(52) **U.S. Cl. .... 257/2; 257/E47.001**(76) **Inventors:** **Jiutao Li**, Boise, ID (US); **Keith  
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**Washington, DC 20006-5403 (US)**(21) **Appl. No.: 12/073,057**(22) **Filed: Feb. 28, 2008****Related U.S. Application Data**(63) Continuation of application No. 10/230,279, filed on  
Aug. 29, 2002, now Pat. No. 7,364,644.(57) **ABSTRACT**

A method of sputter depositing silver selenide and controlling the stoichiometry and nodular defect formations of a sputter deposited silver-selenide film. The method includes depositing silver-selenide using a sputter deposition process at a pressure of about 0.3 mTorr to about 10 mTorr. In accordance with one aspect of the invention, an RF sputter deposition process may be used preferably at pressures of about 2 mTorr to about 3 mTorr. In accordance with another aspect of the invention, a pulse DC sputter deposition process may be used preferably at pressures of about 4 mTorr to about 5 mTorr.



Pulse DC  $\text{Ag}_2\text{Se}$  sputter deposition at different pressure. (a) 20mTorr deposition, (b) 10mTorr deposition, (c) 3mTorr deposition.

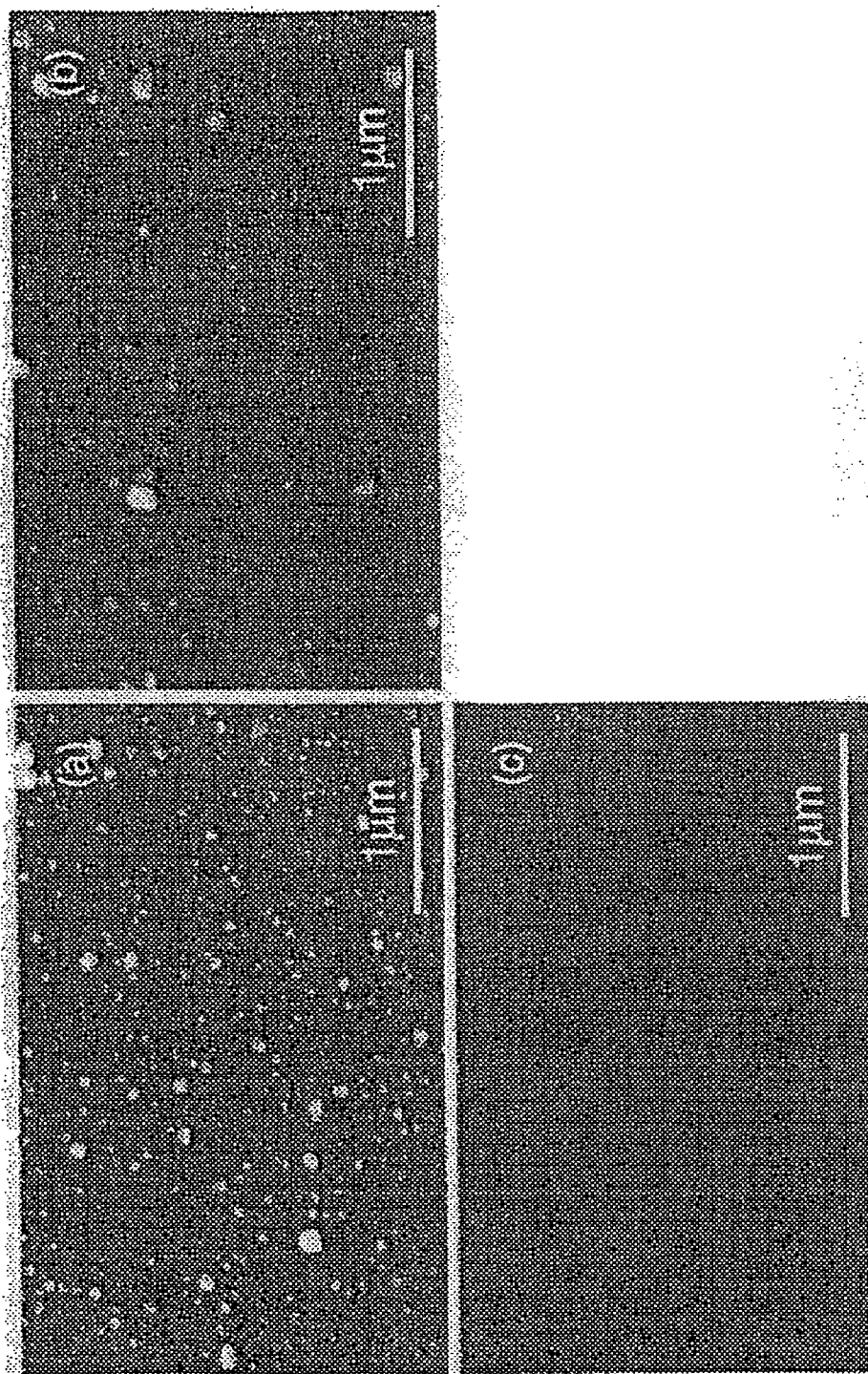


Fig. 1 Pulse DC  $\text{Ag}_2\text{Se}$  sputter deposition at different pressure. (a) 20mTorr deposition, (b) 10mTorr deposition, (c) 3mTorr deposition.

## SILVER SELENIDE FILM STOICHIOMETRY AND MORPHOLOGY CONTROL IN SPUTTER DEPOSITION

### FIELD OF THE INVENTION

[0001] The invention relates to the field of resistance variable memory devices formed using a chalcogenide glass and, in particular, to an improved method of depositing a silver-selenide film on a chalcogenide glass.

### BACKGROUND OF THE INVENTION

[0002] Chalcogenide materials are presently of great interest for use in resistance variable memory devices compared to memory technologies currently in use, due to potential advantages in switching characteristics, non-volatility, memory speed, reliability, thermal characteristics, and durability. Research in this area is reported in the articles "High Speed Memory Behavior and Reliability of an Amorphous  $\text{As}_2\text{S}_3$  Film doped with Ag" by Hirose et al., Phys. Stat. Sol. (1980), pgs. K187-K190; "Polarity-dependent memory switching and behavior of Ag dendrite in Ag-photodoped amorphous  $\text{As}_2\text{S}_3$  films" by Hirose et al., Journal of applied Physics, Vol. 47, No. 6 (1976), pgs. 2767-2772; and "Dual Chemical Role of Ag as an Additive in Chalcogenide Glasses" by Mitkova et al., Physical Review Letters, Vol. 83, No. 19 (1999), pgs. 3848-3851, the disclosures of which are incorporated herein by reference.

[0003] In many memory cell designs employing chalcogenide materials, a film of silver-selenide ( $\text{Ag}_2\text{Se}$ ) is incorporated with a chalcogenide material layer. The silver-selenide film is important for electrical performance. Accordingly, silver-selenide deposition is an important aspect of fabricating the resistance variable memory device. Most available research in silver-selenide deposition is limited and evaporation deposition is normally chosen for silver-selenide film formation.

[0004] Silver-selenide deposition by evaporation has an attendant problem because the dissociative properties of silver-selenide make it impossible to achieve precision stoichiometries of silver-selenide. It is believed that in evaporation techniques, as the silver starts to diffuse to a lower concentration, it begins to agglomerate. As the silver is tied up in clusters or agglomerates, selenium is more readily available for evaporation in the beginning of the evaporation process. Thus, during evaporation techniques, selenium is evaporated more quickly, causing the deposition target to become silver-rich. Near the end of the evaporation process little to no selenium is left for deposition onto the substrate, leaving mostly silver available for deposition. Thus substantial amounts of selenium are deposited on the substrate followed by deposition of primarily silver. Accordingly, the evaporation technique therefore does not uniformly deposit the silver-selenide and controlling the stoichiometry and surface morphology of evaporated silver-selenide is difficult.

[0005] Furthermore, evaporation deposition is not conducive to industrial application. Sputter deposition is more readily available for industrial processes and sputter deposition has many advantages compared to evaporation deposition techniques. For example, sputter deposition provides better film thickness and quality control.

[0006] Generally, sputter deposition, or sputtering, is performed by placing a substrate in a deposition chamber which is evacuated or pressurized to a desired pressure. A particle

stream of the film material usually generated from a target is then generated within the chamber and the deposition occurs by condensation of the particles onto the substrate. In another sputtering technique, often referred to as ion beam bombardment sputtering, a high-energy source beam of ions is directed toward the target. The force of the bombarding ions imparts sufficient energy to the atoms of the target to cause the energized atoms to leave the target and form a particle stream. The resulting deposition upon the substrate forms a thin film.

[0007] Due to the high diffusion property of silver, low melting point of selenium, and the memory properties of silver-selenide, controlling the stoichiometry and morphology of the silver-selenide film during sputter deposition is difficult. For instance, silver-selenide bulk material is conductive, but its conductivity (about thousands  $\text{ohm}^{-1} \text{cm}^{-1}$ ) is relatively lower than that of most metals. Also, silver concentration is critical for electrical performance of the device, thus it is necessary to maintain the silver concentration close to about 66.7 atomic weight percent (herein after represented "%"). With silver concentrations higher than about 67.5%, many nodular defects are formed in and/or on the silver-selenide film. The size of these defects can be about a tenth of a micrometer, which could have severe negative impact on sub micron device fabrication. Although the exact mechanism by which these defects are formed are unknown, it is believed that these defects are caused by excess silver, beyond the desired stoichiometric silver concentration requirements of the silver-selenide film.

[0008] It would be desirable to have an improved method of depositing a silver-selenide film. It would also be desirable to have a method of controlling the stoichiometry and morphology of silver-selenide for sputter deposition.

### BRIEF SUMMARY OF THE INVENTION

[0009] An exemplary embodiment of the present invention includes a method of depositing a silver-selenide film on a substrate. The method includes using a low pressure sputter deposition process. Preferred sputter deposition processes include RF sputtering or pulse DC sputtering. Preferably, the sputter deposition will occur in pressures ranging from about 0.3 mTorr to about 10 mTorr. The invention is particularly useful for depositing a silver-selenide film with better stoichiometric precision. The invention is also particularly useful for sputter depositing a silver-selenide film while avoiding nodular defect formation throughout and on the surface of the silver-selenide film.

[0010] These and other features and advantages of the invention will be better understood from the following detailed description, which is provided in connection with the accompanying drawings.

### BRIEF DESCRIPTION OF THE DRAWINGS

[0011] FIG. 1(a) is an SEM image of a pulse DC sputter deposited silver-selenide film deposited using a pressure of 20 mTorr.

[0012] FIG. 1(b) is an SEM image of a pulse DC sputter deposited silver-selenide film deposited using a pressure of 10 mTorr.

**[0013]** FIG. 1(c) is an SEM image of a pulse DC sputter deposited silver-selenide film deposited using a pressure of 3 mTorr.

#### DETAILED DESCRIPTION OF THE INVENTION

**[0014]** In the following detailed description, reference is made to various specific structural and process embodiments of the invention. These embodiments are described with sufficient detail to enable those skilled in the art to practice the invention. It is to be understood that other embodiments may be employed, and that various structural, logical and electrical changes may be made without departing from the spirit or scope of the invention.

**[0015]** The term “silver-selenide” is intended to include various species of silver-selenide, including some species which have a slight excess or deficit of silver, for instance,  $\text{Ag}_2\text{Se}$ ,  $\text{Ag}_{2+x}\text{Se}$ , and  $\text{Ag}_{2-x}\text{Se}$ .

**[0016]** The term “chalcogenide glass” is intended to include various composition structures based on elements from Group VIA (S, Se, Te, Po, O) alone or in combination with elements from group IV (Si, Ge) and/or group V (P, As, Sb, Bi).

**[0017]** The present invention relates to a process for depositing silver-selenide. In accordance with the invention, low pressures, of for example, 0.3 mTorr to about 10 mTorr, are used to sputter deposit silver-selenide. Also in accordance with the invention, silver-selenide is preferably deposited using an RF sputtering process or pulse DC sputtering process.

**[0018]** Silver-selenide itself has electrical memory properties, i.e. conductivity, and sputter deposition processes normally involve strong current, voltage and ion bombardment. Therefore, both electrical and thermal effects from the sputter deposition process can influence the silver-selenide sputter target and deposited silver-selenide film. For the above reason, sputter deposition requires consideration on how to apply electrical power to silver-selenide targets.

**[0019]** Since the conductivity of silver-selenide is relatively lower than that of most metals, D.C. sputtering has not worked. Regular DC magnetron sputtering attempts have not been effective, primarily because the plasma is not easily ignited.

**[0020]** Depending on the target age, sputter deposition at higher pressures, e.g., about 20 mTorr or greater, result in films with either lower or higher silver concentrations than the desired stoichiometric silver concentration of about 66.7%. It has been observed that high pressure deposition, e.g., about 20 mTorr or greater, of relatively new targets using RF or pulse DC magnetron sputter deposition result in silver-selenide films having silver concentrations of only about 60%, which is much lower than the desired stoichiometric silver concentration of 66.7%. It has also been observed that high pressure deposition, e.g., about 20 mTorr or greater, of relatively old targets using RF or pulse DC magnetron sputter deposition result in silver-selenide films having silver concentrations higher than about 67.5%.

**[0021]** The inventors have discovered that RF or pulse DC magnetron sputter deposition processes at low pressures ranging from about 0.3 mTorr to about 10 mTorr may be used to deposit more precise stoichiometric silver-selenide films while avoiding nodular defects formation in the film. It has also been discovered that the silver-selenide target composition changes over the lifetime of the target, and that the use of

a low pressure sputter deposition process allows for precise stoichiometric deposits from both old and new silver-selenide targets.

**[0022]** FIG. 1 shows SEM images of substrates formed of production grade silicon wafers with silicon nitride films having a pulse DC sputter deposited silver-selenide film of about 500 Angstroms thick. The silver-selenide films shown in FIG. 1 were pulse DC sputter deposited using a Denton Vacuum Discovery® 24 at 200 kHz with a 1056 ns pulse width, and a constant power supply of 150 W. A silver-selenide target having a stoichiometric silver concentration of about 66.7% was used to deposit the silver-selenide film. Comparing the SEM images of the pulse DC sputter deposited silver-selenide films at various pressures indicate that low pressure sputter deposition ranging from about 0.3 mTorr to about 10 mTorr reduces and eliminates nodular defect formations. It was observed that a silver-selenide film deposited using high pressure, i.e., about 20 mTorr, has a silver concentration higher than about 67.5% and has nodular defect formations on the surface and through out the film as shown in FIG. 1(a); as shown in FIG. 1(b) a deposited silver-selenide film formed using a low pressure of 10 mTorr has relatively few nodular defect formations; and as shown in FIG. 1(c) a deposited film using an even lower pressure of 3 mTorr has a smooth surface with no nodular defects.

**[0023]** In accordance with a first embodiment of the invention, a silver-selenide target is sputter deposited using an RF sputter deposition process at a low pressure ranging from about 0.3 mTorr to about 10 mTorr, and more preferably about 2 mTorr to about 3 mTorr, to provide a silver-selenide film having little to no nodular defects and a silver concentration of about equivalent to the silver concentration of a silver-selenide target used to sputter deposit the silver-selenide film. For example, where a silver-selenide target having a silver concentration of about 66.7% is used in the RF sputter deposition process, the deposited silver-selenide film will have a silver concentration of less than about 67.5% and preferably about 67% and more preferably about 66.7%. A process in accordance with the first embodiment of the invention may be used for silver-selenide targets of any age, while still providing a sputter deposited silver-selenide film having a silver concentration about equivalent to that of the silver-selenide target used to deposit the silver-selenide film.

**[0024]** In a sputtering process in accordance with the first embodiment of the invention, the sputtering deposition generally takes place in a chamber. An initial base vacuum pressure is established first. The initial base vacuum pressure may be any suitable pressure, including pressures higher than about 10 mTorr, which may help ignite the plasma. During the sputtering process, process gas should be maintained at a pressure ranging from about 0.3 mTorr to about 10 mTorr, and preferably ranging from about 2 mTorr to about 3 mTorr. The process gas may be any suitable sputtering process gas, for example, krypton, xenon, helium, neon, argon or combinations thereof. The preferred process gas is argon. Although not wishing to be limited by to any particular amounts of power, power applied during the sputtering process preferably may range, for example, between about 100 watts to about 500 watts and is most preferably about 150 watts. Power density and power requirements may vary and depend on the chosen system or size of the target. For example, targets four inches or larger may require more power. The preferred RF frequency is between about 100 kHz and about

20 MHz and is preferably 13.5 MHz. An exemplary sputter deposition system is the Denton Vacuum Discovery® 24.

**[0025]** In accordance with a second embodiment of the invention, a silver-selenide target is sputter deposited using a pulse DC sputter deposition process at low pressures ranging from about 0.3 mTorr to about 10 mTorr to provide a silver-selenide film having a silver concentration of about equivalent to the silver concentration of a silver-selenide target used to sputter deposit the silver-selenide film. For example, where a silver-selenide target having a silver concentration of about 66.7% is used in the pulse DC sputter deposition process the deposited silver-selenide film will have a silver concentration of less than about 67.5% and preferably about 67% and more preferably about 66.7%. A low pressure of from about 4 to about 5 mTorr is preferred. There is a difference between RF sputter deposition and pulse DC sputter deposition in that for pulse DC sputtering a deposition pressure of from about 4 to about 5 mTorr, produces a deposited silver-selenide film having a silver concentration of substantially equivalent to the silver concentration of the silver-selenide target, for example 66.7%. However, generally low pressure deposition provides smoother sputter deposited silver-selenide films having a more precise silver-selenide stoichiometry. The preferred low pressure used may vary depending on the condition of the target, for example, age of the target.

**[0026]** Similar to the process described above in accordance, with the first embodiment of the invention, the sputtering deposition in accordance with the second embodiment also takes place in a chamber, for example, in a Denton Vacuum Discovery® 24, where a suitable initial base vacuum pressure is established first and a suitable process gas is employed. However, in accordance with the second embodiment, during the sputtering process, the process gas should be maintained at a pressure ranging from about 0.3 mTorr to about 10 mTorr, and preferably ranging from about 4 mTorr to about 5 mTorr. Although not wishing to be limited by to any particular amounts of power, the power applied during the sputtering process preferably may range, for example, between about 100 watts to about 500 watts and is most preferably 150 watts and the preferred pulse DC frequency may range, for example, between about 100 kHz and about 250 kHz and is preferably about 200 kHz. However, power density and power requirements may vary and will depend on the chosen system and/or size of the target. For example, targets four inches or larger may require more power. The pulse width should range from about 1000 ns to about 1200 ns and is preferably about 1056 ns.

**[0027]** Although the exact mechanism to explain the origin of experimental observations is unknown there is a connection between sputter pressure, ion kinetic energy, scattering induced energy reduction, and/or RF and pulse DC plasma electrical properties. For practical application, the inventors propose to use an RF sputter deposition process or pulse DC sputter deposition process at lower pressure to deposit better precision stoichiometric silver-selenide films and avoid nodular defect formations on the film. Accordingly, pressure may be varied within the low pressure range of from about 0.3 mTorr to about 10 mTorr to fine tune the silver concentration of the silver-selenide film. The power sources may be varied as well. This is of great importance in device fabrication in that many devices require elemental concentrations slightly deviated (i.e.,  $\pm 2\%$  at. concentration) from the preferred value of about 66.7%. Accordingly, since low pressure sputter deposition can also be used on relatively old targets while still

providing more precise stoichiometric concentrations of silver, the invention expands the target lifetime thus reducing process costs.

**[0028]** While exemplary embodiments of the invention have been described and illustrated, various changes and modifications may be made without departing from the spirit or scope of the invention. Accordingly, the invention is not limited by the foregoing description, but is only limited by the scope of the appended claims.

**1-75.** (canceled)

**76.** A resistance variable memory device comprising:

a silver-selenide film deposited onto a chalcogenide glass layer, the silver-selenide film deposited using a sputter deposition pressure varying in a range from about 0.3 mTorr to about 10 mTorr, having a formula of  $\text{Ag}_x\text{Se}$ , where  $x$  is about 2, and having substantially no nodular defects.

**77.** The device of claim 76 wherein said silver-selenide film has a silver concentration of less than about 67.5 atomic weight percent.

**78.** The device of claim 77 wherein said silver-selenide film has a silver concentration of about 67 atomic weight percent.

**79.** The device of claim 77 wherein said silver-selenide film has a silver concentration of about 66.7 atomic weight percent.

**80.** A resistance variable memory device comprising:

a silver-selenide film comprising:

a silver-selenide target formed onto a chalcogenide glass layer, wherein the silver-selenide target has a silver concentration of less than about 67.5 atomic weight percent, has the formula of  $\text{Ag}_x\text{Se}$ , where  $x$  is about 2, and has substantially no nodular defects.

**81.** The device of claim 80 wherein said silver-selenide film has a silver concentration of about 67 atomic weight percent.

**82.** The device of claim 81 wherein said silver-selenide film has a silver concentration of about 66.7 atomic weight percent.

**83.** A resistance variable memory device comprising:

a silver-selenide target pulse DC sputter deposited onto a chalcogenide glass layer deposited at a pressure range between about 0.3 mTorr and about 10 mTorr, said silver-selenide target having a silver concentration of about 66.7 atomic weight percent, and

a silver-selenide film having substantially no nodular defects from said sputtered target, the silver-selenide film having the formula of  $\text{Ag}_x\text{Se}$ , where  $x$  is about 2.

**84.** The device of claim 83 wherein said silver-selenide film has a silver concentration of less than about 67.5 atomic weight percent.

**85.** The device of claim 84 wherein said silver-selenide film has a silver concentration of about 67 atomic weight percent.

**86.** The device of claim 84 wherein said silver-selenide film has a silver concentration of about 66.7 atomic weight percent.

**87.** The device of claim 83 wherein said pressure range is between about 4 mTorr and about 5 mTorr.

**88.** A resistance variable memory device comprising:  
a silver-selenide target having a silver concentration of about 66.7 atomic weight percent; and  
a silver-selenide film formed from said sputtered target, said silver-selenide film having the formula of  $\text{Ag}_x\text{Se}$ , where x is about 2 and having substantially no nodular defects.

**89.** A resistance variable memory device comprising:  
a silver-selenide film deposited onto a chalcogenide glass layer, the silver-selenide film having a formula of  $\text{Ag}_x\text{Se}$ , where x is about 2, and having substantially no nodular defects.

**90.** The device of claim **89** wherein said silver-selenide film has a silver concentration of less than about 67.5 atomic weight percent.

**91.** The device of claim **90** wherein said silver-selenide film has a silver concentration of about 67 atomic weight percent.

**92.** The device of claim **90** wherein said silver-selenide film has a silver concentration of about 66.7 atomic weight percent.

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