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A new effective method for thermal annealing of magnetic tunnel junctions in air with protective overlayers

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Thermal annealing is an important process to enhance greatly the tunneling magnetoresistance (TMR) of magnetic tunnel junctions (MTJs). MTJ annealing is conventionally carried out in vacuum below 10^{-5} Torr. However, this method involves the cost and complications of using a vacuum furnace. Pumping and venting a chamber are time-consuming; moreover, the sample temperature is difficult to measure accurately and therefore not easy to control. We have developed a method and an instrument to perform thermal annealing of MTJs in air. The method is based on protective overlayers, and the instrument has a simple structure composed of an air heat gun, thermocouple with feedback control, permanent magnets for magnetic field, and a sample holder. The influence of thermal annealing in air on MTJs properties was studied systematically on Al_2O_3 MTJ samples. The samples are successfully protected from oxidation by using Au/Ru, or Al_2O_3 films as protective overlayers. The Al_2O_3 overlayer can be removed easily with NaOH solution. A MgO MTJ sample was annealed with this technique and its TMR increased from 17.5% to 141.3%.

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I. INTRODUCTION

The ferromagnetic layer adjacent to the insulator in a magnetic tunnel junction (MTJ) may be partially oxidized during the formation of the oxide barrier, thereby degrading the junction performance. The magnetoresistance (MR) ratio can be greatly improved by thermal annealing a MTJ sample.[1] Postdeposition thermal annealing is critical to achieving high tunneling magnetoresistance (TMR). TMRs as high as 361% have been obtained in MTJs with $Co_{40}Fe_{40}B_{20}$ fixed and free layers deposited by sputtering with an exchange-bias structure and postdeposition annealing at 400 °C.[2] The highest TMR ratio obtained so far is 500% in a pseudospin-valve MTJ annealed at 475 °C.[3] There are proposals explaining the TMR enhancing effect of thermal annealing.[4–8] It was suggested to occur because of the movement of oxygen atoms in the ferromagnetic layer to the oxide barrier.[4] Ando *et al.* proposed that the improvement is due to both an increased homogenization of the insulator and a small fluctuation of the tunnel resistance.[7]

The thermal annealing process is usually carried out in a vacuum furnace where a magnetic field up to a few tenths of a tesla (a few thousand Gauss) is applied on a sample during annealing.[8–11] Rapid thermal annealing (RTA) is also commonly employed to anneal MTJ samples.[12–14]

In addition to the cost and complication in using a vacuum furnace and RTA, one of the key challenges in performing thermal annealing of MTJs is accurate measurement and control of the sample temperature. Monitoring the ambient with a thermocouple is not feasible because heat conduction in vacuum is poor and the sample temperature measured depends greatly on the distance between the thermocouple and the sample; moreover, the high temperature ramp rates in RTA prevent the wafer from coming to thermal equilibrium with the process chamber. *In situ* pyrometry is a possible temperature control strategy to implement real time control; however, it will further complicate the chamber design and thus make the annealing process more costly. Also, the emissivity of the MTJ and its substrate is far lower than a blackbody and not well known, making pyrometry unreliable.

In view of this, we have developed a technique and an instrument to carry out thermal annealing of MTJs in air which also enhances a sample's TMR like vacuum annealing does. The major challenge of annealing an MTJ sample in air is the oxidation problem. We found that this problem can be overcome by making use of overlayers[15] such as Au/Ru and Al_2O_3 to protect the MTJ samples from oxidation.

II. EXPERIMENT

The instrument is shown in Fig. 1. The air heat gun can generate hot air up to 500 °C. The sample made of MTJ thin films and protective overlayers on a silicon wafer is placed on the sample holder consists of two wedges with the front sample side facing downward. The hot air will blow toward the back side of the silicon wafer and the heat at the sample back will then be conducted to the front side. Silicon has such a high thermal conductivity that the thermal gradient from front to back is negligible. The thermocouple is fixed in position by the mount and it is pushed into contact with the sample so that the sample temperature can be measured accurately. The annealing temperature can be set at the temperature controller. The temperature controller compares the measured sample temperature and the set annealing temperature and provides a feedback control signal to the phase

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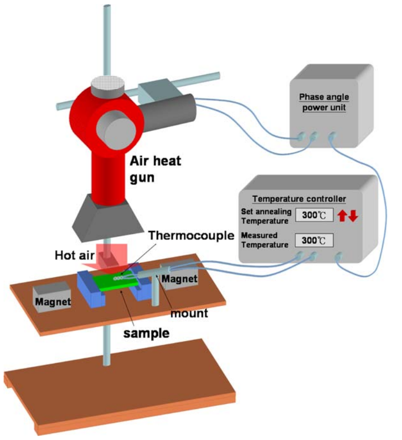

FIG. 1. (Color online) The instrument setup for thermal annealing of MTJs in air. The air heat gun provides the hot air to anneal the sample. The annealing temperature is measured by the thermocouple which is in touch with the sample. According to the measured sample temperature, the temperature controller feedback controls the phase angle power unit to regulate the power supplied to the air heat gun so that the sample is annealed at the targeted temperature.

angle power unit to adjust the power supplied to the air heat gun. If the sample temperature is higher than the set annealing temperature, the temperature controller will signal the phase angle power unit to reduce the power supply duration in each cycle in order to decrease the power to the heat gun and lower the hot air temperature and vice versa. The feedback control mechanism is illustrated in Fig. 2. There are two magnets on the two sides of the sample to provide a magnetic field up to 70 mT (700 Oe). The magnet positions can be adjusted. If smaller magnetic field is needed, they can be moved backward to reduce the field.

MTJ samples were made to test this new technique of thermal annealing in air. MTJ wafers were deposited using dc magnetron sputtering in an ultrahigh vacuum chamber equipped with 11 sputtering targets with a base pressure of 2.67×10^{-8} Pa $(2\times10^{-10}$ Torr). The Al_2O_3 barrier was formed by depositing a layer of metallic Al then oxidizing it in oxygen plasma. A magnetic field of 7 mT (70 Oe) was applied during magnetic layer deposition to induce the easy axis and pinning direction. MTJ junctions were patterned and connected with the top layer of metal lines using photolithography and ion milling. The protective Au/Ru and Al_2O_3 overlayers were deposited in the last step. For the MTJ junctions to be measured by four-probe method, around 100 nm Au/Ru was used as the protective overlayer. For the MTJ wafers to be measured with current-in-plane-tunneling (CIPT) technique, on top of the 7 nm Ru top layer which is required as the top electrode for CIPT measurement, around 10 nm Al_2O_3 protective overlayer was deposited. After annealing, this Al_2O_3 protective overlayer can be easily removed by dipping the sample into a sodium hydroxide solution for a few minutes.

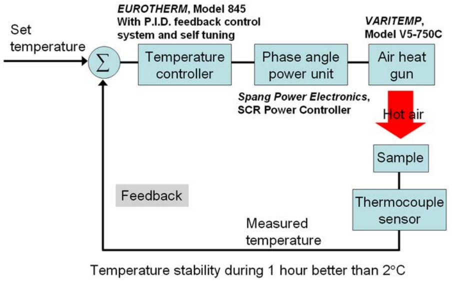

FIG. 2. (Color online) The block diagram of the instrument setup.

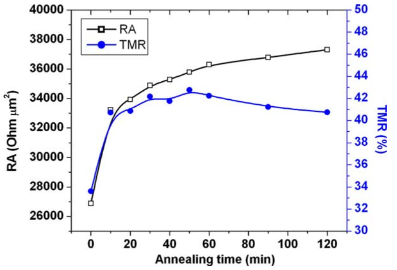

FIG. 3. (Color online) The changes of TMR and RA with annealing time at 280 °C in air. Sample: substrate/2.5Ta/5Au/10IrMn/4CoFe/1 Al:oxidized/5CoFe/5Ta/7Ru/(protective overlayer 140 Au) (units in nanometers).

III. RESULTS AND DISCUSSION

MTJ junctions with the structure of substrate/2.5 Ta/5 Au/10 IrMn/4 CoFe/preoxidation; 1 Al:oxidized/5 CoFe/5 Ta/7 Ru/(protective overlayer 140 Au) (units in nanometers) were fabricated and thermally annealed in air in the setup, as shown in Fig. 1. Annealing was carried out at several different temperatures and we found that 280 °C gave the best annealing results for these Al_2O_3 MTJs. The TMR and *RA* of the sample were measured by four-point measurement at room temperature. Figure 3 shows the variation of the TMR and *RA* of the sample with the annealing time. Without annealing, the sample exhibited a TMR value of 34% and *RA* value of 27 $k\Omega\ \mu m^2$. The TMR and *RA* values increased to 41% and 33 $k\Omega\ \mu m^2$ after 10 min of annealing in air. The result indicates that the protective Au overlayer successfully protected the MTJ sample from oxidation during thermal annealing in air. This enhancement effect on the TMR is typically shown in thermal annealing in vacuum[16,17] which suggests that thermal annealing in air has similar effect to the sample as annealing in vacuum. For longer annealing times of up to 50 min, the TMR and *RA* values rose steadily to 43% and 36 $k\Omega\ \mu m^2$, respectively. Annealing time longer than 50 min started to reduce the TMR while *RA* continued to increase.

In addition to Au, we have also experimented with Ru protective overlayer. MTJ junctions with the structure of substrate/2.5Ta/2.5Au/10IrMn/4CoFe/1 Al:oxidized/5CoFe/5Ta/7Ru/(protective overlayer 90 Au/20 Ru) (units in nanometers) was fabricated. In this sample, the protective overlayer was composed of 90 Au and 20 Ru. Ru is an appropriate choice as a protective overlayer because ruthenium oxide is also conductive. Before annealing, the TMR and *RA* values were 27% and 15 $k\Omega\ \mu m^2$, respectively. This sample was then annealed in air for 60 min at 280 °C and the TMR and *RA* increased to 35% and 18 $k\Omega\ \mu m^2$, respectively. The result shows that 90 Au/20 Ru can also effectively protect the MTJ from oxidation during thermal annealing and enable the annealing to take effect on the TMR and *RA* values of the sample.

From the above results, we can conclude that MTJ junctions with protective overlayers of Au/Ru can also undergo the same TMR enhancement process through thermal annealing in air. To further demonstrate the applicability of this thermal annealing in air of MTJs with protective overlayer technique, we prepared a MTJ wafer for CIPT measurement.[18] The CIPT measurement is a good test for the technique because the CIPT has strict requirement on the top sheet resistance (R_T). Unlike a regular four-probe measurement where a macroscopic probe is used, the CIPT measurement uses a probe which is microscope in size. If the top electrode of the MTJ becomes oxidized during the annealing and its resistance changes significantly, the microscopic CIPT probe will not be able to obtain stable electrical contact with the wafer and the CIPT instrument will fail to carry out the TMR measurements.

A MTJ wafer with the structure of substrate/2.5Ta/5Au/10IrMn/4CoFe/1 Al:oxidized/5CoFe/5Ta/7Ru(units in nanometers) was made. A CIPT measurement (Capres, Denmark) was then carried out. The R_T was found to be around 36 Ω/sq. The TMR and *RA* values were measured to be 20% and 6 kΩ μm^2, respectively. The wafer was then cut up into two pieces. One of them was annealed in air at 280 °C for 30 min. After annealing, we tried to perform CIPT measurement on it but the probe could not obtain stable electrical contact with the sample and the measurement failed. It might be because the top Ru layer was oxidized during annealing and became more resistive and its surface became rough, and therefore the microscopic CIPT probe could not come into good contact with the sample. On the other hand, the other wafer piece was deposited with 10 nm Al_2O_3 protective overlayer in the chamber, and it was annealed in air at 280 °C for 30 min. The wafer piece was then dipped into a concentrated solution of sodium hydroxide solution for 10 min to remove the Al_2O_3 protective overlayer. X-ray photoemission spectroscopy was used to make sure there was no Al_2O_3 left on the wafer surface. This time the CIPT probe could obtain good electrical contact and the CIPT measurement was carried out. R_T did not change much by the annealing and it was measured to be around 33 Ω/sq, while the TMR and *RA* values increased to 26% and 8 kΩ μm^2, respectively. This result shows that with the Al_2O_3 protective overlayer protecting the top Ru layer, thermal annealing in air can also enhance the TMR value of a MTJ wafer for CIPT measurement. A study between the percentage of successful CIPT probe contact and the thickness of the Al_2O_3 protective overlayer was carried out, and the result is shown in Fig. 4. 10 nm Al_2O_3 protective overlayer was found to be the minimum thickness sufficient to protect the MTJ wafer. We repeated the same annealing procedure to a MgO MTJ wafer for CIPT measurement. The structure of the wafer is substrate/2.5Ta/10Au/10IrMn/4CoFe/0.8Ru/10CoFeB/0.4Mg/2.5Mg:oxidized/1.5CoFeB/5Ta/7Ru(units in nanometers). Several annealing temperatures were tried and it was found that 400 °C works the best for MgO MTJ samples. Before annealing, the MgO MTJ wafer shows *RA* of 365 kΩ μm^2 and TMR of 17.5% as measured by the CIPT. After annealing at 400 °C for 30 min in air, its *RA* and TMR increased to 1.2 MΩ μm^2 and 141.3%, respectively. In order to further demonstrate the validity of the air annealing technique, another wafer of the same MgO MTJ structure was annealed in 10^{-5} Torr vacuum for comparison. The best TMR was obtained after vacuum annealing at 350 °C (instead of 400 °C for annealing in air) for 30 min. The *RA* and TMR increased to 265 kΩ μm^2 and 125%, respectively. The differences in the optimum annealing temperatures and the increases of the *RA* and TMR by the two annealing methods were attributed to the fact that the annealing temperature in vacuum is relatively difficult to measure and control with the same accuracy as in annealing in air.

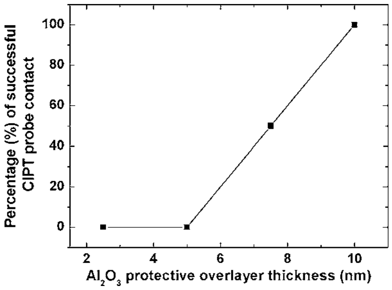

FIG. 4. The dependence of the percentage of successful CIPT probe contact on the thickness of the Al_2O_3 protective overlayer.

IV. CONCLUSION

In conclusion, we have developed a technique of thermal annealing of MTJs in air with protective overlayers which can increase the TMR values of the junctions. Using Au/Ru as the protective overlayers on the MTJs for regular four-probe measurement, the technique was demonstrated to increase the TMR values. The technique is also applicable for CIPT measurement by using Al_2O_3 protective overlayer. This method has these advantages: (1) time efficient with no pumping and venting required because no vacuum is needed, (2) annealing temperature can be controlled much more accurately because the heat conduction in air is much better than in vacuum, (3) simple and low cost as the instrument involved is simple to set up, and (4) suitable for both patterned MTJs for four-probe measurement and wafers for CIPT measurement.

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