International Journal of Thin Film Science and Technology

Volume 6
Issue 3 *Sep. 2017*

Article 6

2017

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International Journal of Thin Films Science and Technology

http://dx.doi.org/10.18576/ijtfst/060306

Effect of Cobalt Silicide Buffer Layer on Magnetic and Electrical Properties of Co Thin Films Deposited on Si, GaAs and Glass Substrates

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Received: 2 Jul. 2017, Revised: 25 Aug. 2017, Accepted: 29 Aug. 2017.
Published online: 1 Sep. 2017.

Abstract: Cobalt silicide layers have been grown by E–beam evaporation of Co onto Si (100) substrate and subsequent thermal treatment at 673K for 5 hours. A fresh layer of 100 nm Co is deposited on the silicide layer (sample–1). A thin layer of 5 nm Co have been deposited on GaAs (100) substrate and annealed at 673K for 5 hours. A fresh layer of 100 nm Co is deposited on 5 nm annealed Co buffer layer (sample–2). 100 nm Co films have been grown on glass substrate for comparison. Magnetic properties of Co thin films have been studied by Vibrating sample magnetometer (VSM). Measurements of magnetic properties show that the coercivity is 580 Oe for sample–1. The coercivity of the sample–2 is 240 Oe. The coercivity of 100 nm as-deposited Co films on glass substrate is only 50 Oe and the coercivity increases up to 100 Oe after annealing at 673K for 5 hours. Electrical measurements show that the Sample-1 is metallic in nature but the Sample–2 is semiconducting in nature. In X-ray diffraction measurement, the Co films grown on n-GaAs and Si substrates exhibited a polycrystalline hcp structure. XRD study of Co thin films grown on glass substrate show a microcrystalline hcp structure.

Keywords: Cobalt silicide, Co/Si, Co/GaAs, Buffer layer, Magnetization, Coercivity, Annealing

1 Introduction

The interaction of cobalt atoms with surface atoms of Si substrate leads to the formation of cobalt silicide. Cobalt thin films and their silicides have been studied extensively during the past decades due to their importance in contact materials in microelectronics as well as spintronic applications [1]. Magnetic properties, such as magnetic hysteresis, coercivity, magnetic anisotropy, magneto resistance as well as structure of the magnetic domain, are modulated by the interface between thin film and substrate, surface roughness and silicide at the interface [2–7]. It is observed that the interfacial resistance at the interface between ferromagnetic thin film and substrate influences the coercivity as well as shape of the hysteresis loop [2]. The well-known prototype of spintronics device is the spin FET proposed by Datta and Das [8], which has yet to be realized practically. The generation of sufficient spin polarized current from ferromagnetic to semiconductor is the main difficulties for Spin FET implementation. High spin injection efficiency has been achieved from a ferromagnetic metal into a paramagnetic metal [8]. But the spin injection from ferromagnet into semiconductor remains a challenging task [9]. Direct spin injection across ferromagnet (FM)/semiconductor (SE) yields an spin injection efficiency of the order of 1 percent [10–11]. This is due to the fact that the conduction electrons in the ferromagnet is highly spin polarized. Difference in density of states at the Fermi level make highly spin polarization in ferromagnet. The basic reason for the low spin injection efficiency from ferromagnetic metal into semiconductor is the conductivity mismatch between them. The high value of resistivity of semiconductor limits the spin dependent effect at the interface. Depending on the resistivity of ferromagnetic metal and semiconductor, it is theoretically shown that the spin injection efficiency $\eta \propto \left({}^{\sigma_{SC}}/_{\sigma_{FM}}\right) \ll 1$, where σ_{SC} and σ_{FM} are the conductivities of semiconductor and ferromagnetic metal, respectively [12]. This change in device magnetoresistance (~ 0.1 %) in parallel and anti-parallel is very small and unsatisfactory for practical device application. Interfacial resistance at the boundary of FM/SE interface is vital requirement for the efficient spin injection and magneto resistive effect in FE/SE junction. Cobalt silicide buffer layer not only enhance the crystal quality of Co thin film but also increase the magnetic anisotropies [13].

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They have also shown that few $CoSi_2$ monolayer can prevent the interdiffusion of Si and Co atoms. Cobalt−silicon hybrid system is of particular interest in the field of spintronics because cobalt has high spin polarization at room temperature and Si has long spin coherence length (longer than micrometer) [9,14]. Any structural disorder at the interface in hetero structure of Co on Si can drastically reduce the spin injection efficiency [15–18]. If a small amount of Co diffuses into the Si substrate, each Co atom carry some magnetic moment and oriented randomly in the Si. The diffused Co into the Si have random magnetic moment with respect to the magnetic moment of the Co thin film. These scattered Co may scatter the injected carriers and hence reduce the spin injection efficiency [18]. Thus, in order to control and improve the interface, special treatments of the interface are necessary.

A theoretical drift-diffusion transport model reveals that the presence of interfacial resistance (IR) between ferromagnetic metal and semiconductor can increase the spin-injection efficiency and magneto resistance ratio in FM/SC system [19]. It has been shown that the presence of IR at the FM/SE interface is crucial for the generation of large spin splitting of electrochemical potential and consequently a high spin injection efficiency η. Relatively large value of interfacial resistance comparable to the resistance of semiconductor can increase the spin injection efficiency from 1% to 30%.

In this paper, the cobalt silicide ($a = 0.5365$ nm) layer is chosen as a buffer layer, due to its relatively small lattice mismatch (~1.2%) with Si ($a = 0.5431$ nm) substrate and its wide application at the primary contact and narrow gate electrode. The net magnetic moment of silicide buffer layer is zero and no effect on the magnetic properties of co thin films, which is important in combination of the magnetic materials and semiconductor materials. The effect of cobalt silicide on the electrical and magnetic properties are investigated and presented in this paper. In X-ray diffraction measurement, the Co films grown on a n-GaAs (0 01) substrate exhibited a polycrystalline hcp structure.

2 Experimental Details

Co thin films have been prepared on Si (100), GaAs (100) and glass substrates using E-beam evaporation technique. Before the start of the deposition, glass substrates were cleaned by dipping the substrates in a solution of chromic acid which is a mixture of potassium dichromate ($K_2Cr_2O_7$) and sulfuric acid (H_2SO_4). Then the substrates have been cleaned with distilled water and dried. The Si-doped GaAs (100) substrate having electron concentration of 10^{24}m^{-3} is used in this research. Si substrate was p-type. All the substrates are placed in an ultrasonic bath with acetone to remove final contamination and then dried. The native oxide layers of Si substrates were removed with H_2O_2 (30 % solution). Few nanometer (~ 5 nm) Co thin film is deposited on both Si and GaAs substrates. The films are annealed at 673K in a heavy-duty oven for 5 hours in open air. Finally, a fresh layer of 100 nm Co thin film is deposited on the 5 nm annealed Co film. The final structure becomes 100 nm Co / 5 nm annealed Co / Si (100). This sample is called sample–1. Another sample structure become 100 Co / 5 nm annealed Co / GaAs (100). This sample is called sample–2. Thin films of 100 nm Co are also deposited on glass, Si (100) and GaAs (100) substrates for comparison. Vibrating Sample magnetometer is used to study the magnetization process of the samples at room temperature. Four−probe method is used to measure the electrical properties of samples.

3 Results and Discussion

It is known that the interface between ferromagnetic metal and semiconductor substrate influences many magnetic properties such as magnetization process, coercivity, magnetic anisotropy constant and magnetoresistance. The hexagonal closed pack (hcp) is the most stable phase of Co at room temperature.

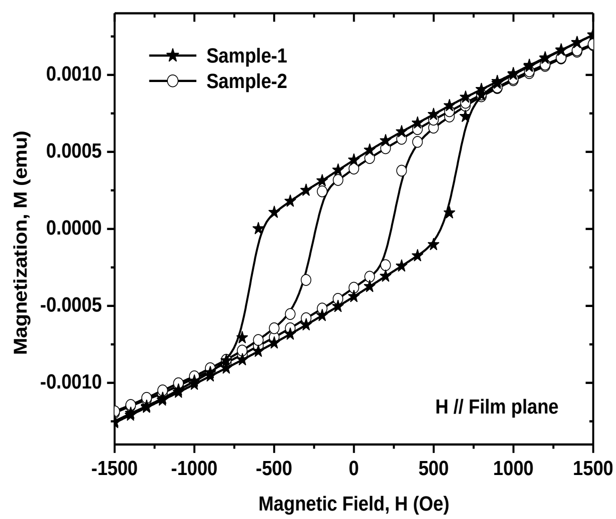

Figure 1. Magnetization processes of sample-1 (100 nm as-deposited Co film/5 nm annealed Co layer/Si substrate) and sample-2 (100 nm as-deposited Co film/5 nm annealed Co layer/GaAs substrate). The applied magnetic field was parallel to the film plane and measurement was carried out at room temperature.

Cobalt reacts with silicone substrate and forms cobalt silicide at the interface. Cobalt silicide is a non-magnetic alloy whose resistivity is much larger than the resistivity of ferromagnetic metal cobalt. But the resistivity of cobalt silicide is less than the resistivity of silicon substrate. The magnetic properties such as coercivity of cobalt thin films is enhanced not only by the interface but also by the interfacial resistance between Co thin films and underlying silicon substrate. To study the effect of interfacial resistance on the magnetic properties of Co thin films on silicon substrate, sample-1 and sample-2 are prepared and their magnetic properties are studied by VSM at room temperature. The magnetization processes of 100 nm as-deposited Co thin films on 5 nm annealed cobalt buffer (cobalt silicide) layer on Si and GaAs substrates are shown in figure-1. It is evident from the graph that the coercivity of 100 nm Co thin film on cobalt silicide buffer layer (sample-1) is enhanced. The coercivity of sample-1 is 580 Oe. On the other hand, the coercivity of same thick Co thin film on 5 nm annealed buffer layer (sample-2) is only 240 Oe. Co thin films of 5 nm are deposited on Si and GaAs substrate. These are annealed at 673K for 5 hours in open air. Cobalt silicide is formed in the case of Co thin film on Si substrate. On the other hand, CoGa intermetallic compound and Co_2GaAs ternary phase are formed in the case of Co thin films on GaAs substrate.

A uniform buffer layer of cobalt silicide is formed on Si substrate. It is known that annealing at high temperature can crystallites films and increase the coercivity [20]. A microcrystalline Co film on the top surface of the cobalt silicide buffer layer can increase the coercivity of Co thin films. It is also known that the lattice mismatch between cobalt silicide and Si substrate is about 1.2 %. Interfacial dislocation occurs at the interface of cobalt silicide and Si substrate. It can be a reason of higher coercivity of the sample–1.

An intermetallic compound CoGa is formed during the annealing of Co thin films on GaAs substrate. Annealing at high temperature can form Co2GaAs ternary phase at the interface between fresh 100 nm Co film and GaAs substrate [21]. The reduced coercivity and magnetization of sample-2 are attributed to the formation of Co2GaAs ternary phase at the interface. Co atoms consume and forms cobalt silicide during high temperature annealing. To study the effect of cobalt silicide buffer layer on the magnetic properties of Co thin films, 100 nm cobalt thin film is deposited on Si (100) substrate and annealed at 673K for 5 hours in open air. The magnetization processes of this sample and sample–1 is shown in figure–2.

It is evident from the figure that both the magnetization and coercivity of 100 nm annealed sample on Si substrate are low. In the case of sample–1, initially5 nm Co layer is grown on Si substrate and annealed at high temperature. It is expected that almost all the Co atoms are consumed and formed cobalt silicide buffer layer. Therefore, fresh 100 nm Co thin film grown on cobalt silicide buffer layer has higher magnetization value than 100 nm annealed Co thin film grown on bare Si substrate. The larger values of magnetization and coercivity of sample–1 can be attributed to the formation of buffer layer between fresh 100 nm Co thin film and Si substrate. It is expected that the higher value of anisotropy energy is responsible for high coercivity. Therefore, the formation of cobalt silicide buffer layer in sample–1 is responsible for increased coercivity of this sample.

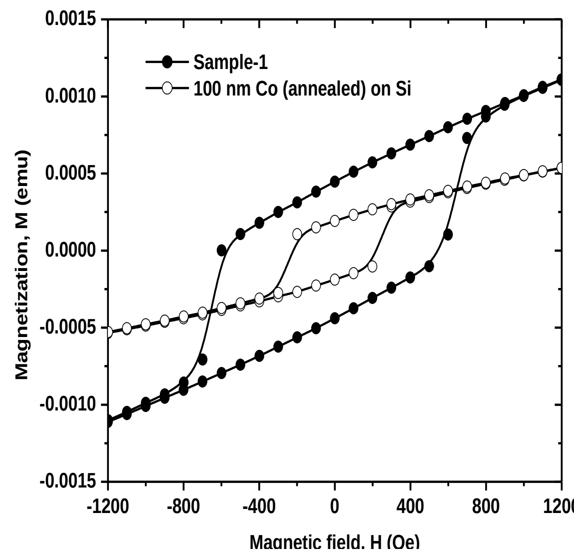

Figure 2. The magnetization processes of sample-1 and 100 nm Co film on Si substrate (annealed at 673K for 5 hours in open air).

Magnetic thin films of cobalt have been deposited on glass substrate is microcrystalline in nature [22]. The magnetization process of both the as-deposited and annealed Co thin films on glass substrate is shown in figure–3. It is well known that the coercivity and the shape of hysteresis loop depends on the grain size of the deposited films. For as-deposited films, the expected grain size are very small and randomly oriented inside the film. Therefore, relatively large value of magnetic field is required to saturate the sample. The coercivity of 100 nm as-deposited Co thin film on glass substrate is about 50 Oe. The coercivity becomes 100 Oe after annealing and relatively a small magnetic field is required to saturate the sample. It is known that the grain size of Co thin films increases after annealing [23].

It is well known that when the crystal grains are large, crystalline magnetic anisotropy is large and magnetization in each crystal grain orients in different directions, because easy axes are not parallel to each other [24]. Therefore, larger grain size can lead to a large coercivity in Co/GaAs and Co/Si systems than Co/glass thin films. The coercivity of annealed thin films is increased due to the formation of larger grain after annealing.

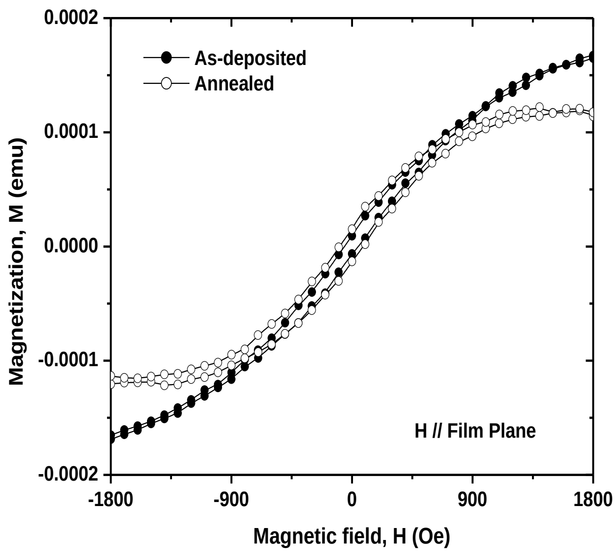

Figure 3. The magnetization process of Co thin films on glass substrate. The magnetic field was parallel to the film plane.

Cobalt atoms can interact with Si substrate and forms a series of cobalt silicide including Co_3Si, Co_2Si, CoSi, and $CoSi_2$, which are promising compounds for use in solid state electronics and spintronics [25]. In the present study, a 5 nm layer of Co thin film is deposited and annealed at high temperature to form cobalt silicide. A fresh layer of 100 nm Co is deposited on this cobalt silicide buffer layer. The electrical properties of this fresh layer are measured and its temperature dependent resistivity is shown in figure–4. It is seen from the figure that the resistivity increases almost linearly above 80 °C. At low temperature, the value of resistivity decreases with the increase in temperature. Cobalt silicide is an intermetallic compound and shows semiconducting behavior at low temperature.

In this temperature range (30–70 °C), the rate of increase in resistivity of 100 nm Co thin film is lower than the rate of decrease in resistivity of cobalt silicide. Therefore, at low temperature the sample behaves as a semiconductor.

Co atoms can interact with GaAs substrate at high temperature and lead to the formation of Co_2GaAs [21]. For sample–2, 5 nm Co is deposited and annealed at 673K for 5 hours in open air. Therefore, it is expected that Co_2GaAs is formed at the interface between fresh 100 nm Co thin film and GaAs substrate. The variation of resistivity with respect to temperature of sample–2 is shown in figure–5. It is seen from the figure that the resistivity of sample–2 decreases with the increase in temperature. Co_2GaAs is semiconductor and it shows negative temperature coefficient of resistance (TCR). Top 100 nm Co layer is as–deposited metallic cobalt. Therefore, the negative TCR of ternary phase Co_2GaAs is higher than the positive TCR of 100 nm fresh cobalt layer.

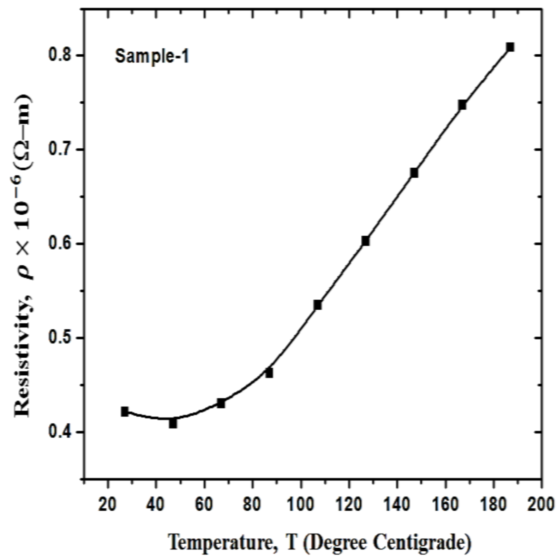

Figure 4. Variation of resistivity of sample–1 with respect to temperature.

To study the effect of annealing on the electrical properties of 100 nm Co thin film on GaAs substrate, 100 nm as-deposited Co thin film is prepared on bare GaAs substrate. The resistivity of as-deposited 100 nm Co thin film on GaAs substrate is shown in figure–6. It is clear from the figure that TCR of the sample is positive.

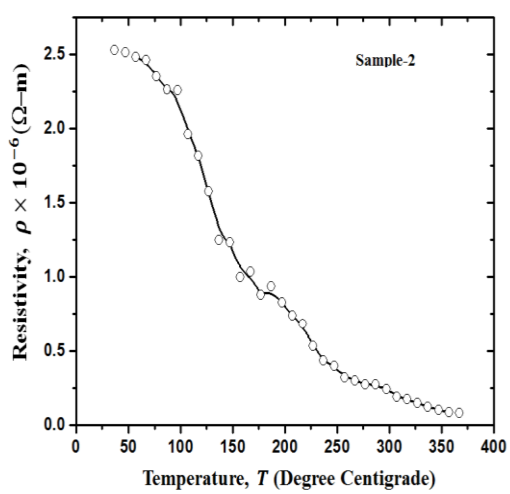

Figure 5. Variation of resistivity of sample–2 with respect to temperature.

GaAs substrate is Si-doped having electron concentration of $10^{24}m^{-3}$.Therefore, it shows negative TCR in the temperature range 25–125 °C. Ionization takes place in the temperature range. It is also clear from the figure that ionization is completed at about 125 °C. In the same temperature range, the top 100 nm Co thin film is metallic and show positive TCR. The negative TCR of GaAs substrate is much more than the positive TCR of Co thin films. The overall resistivity of the sample shows little bit negative TCR in the temperature range 25–125 °C. The sample shows positive TCR above 125 °C because the negative TCR becomes almost zero after complete ionization of donor in GaAs sample.

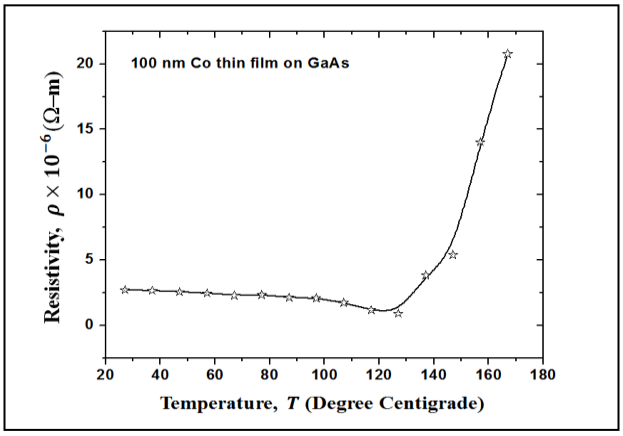

Figure 6. Variation of resistivity of 100 nm Co thin film on bare GaAs substrate with respect to temperature.

4 Conclusions

The magnetization and coercivity of Co thin films are enhanced due to the presence of cobalt silicide buffer layer between as-deposited Co thin films and substrate. But the magnetization and coercivity of Co thin films are decreased considerably as the film is annealed at high temperature in open air. High value of anisotropy field in sample-1 is responsible for higher value of coercivity. XRD measurement reveals that Co thin films are polycrystalline in nature on Si and GaAs substrate but it is microcrystalline in nature on the glass substrate. Co thin films with very small grain on glass substrate is responsible for small coercivity. As-deposited 100 nm Co thin film on cobalt silicide buffer layer shows metallic behavior (sample–1) because intermixing is less between fresh Co thin films and cobalt silicide buffer layer. But sample–2 shows semiconducting behavior due to the formation of ternary phase Co2GaAs. On the other hand, the 100 nm as-deposited Co thin film prepared on bare GaAs substrate show semiconducting behavior at low temperature due to the ionization of dopants. The same sample show metallic behavior at high temperature because positive TCR of top 100 nm Co thin films.

Acknowledgements

This work was partially supported by the financial support from National Science and Information & Technology (NSICT) Fellowship, Provided by the Ministry of Science and Information & Technology, Government of Bangladesh. The authors would like to thank Atomic Energy Commission, Dhaka and Central Science Laboratory, University of Rajshahi for providing experimental support.

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