Nuclear Instruments and Methods in Physics Research B 412 (2017) 41–45

Contents lists available at ScienceDirect

Nuclear Instruments and Methods in Physics Research B

journal homepage: www.elsevier.com/locate/nimb

Controlled oxidation state of silver oxide thin films deposited by an integrated anode layer ion source ion beam sputter module

Ching-Hsiu Chen [a], Yu-Ling Huang [a], Kai Huang [a], Ejigu Assamen Ayalew [a], Liang-Chiun Chao [a,*], Jin-Ping Ao [b]

[a] Graduate Institute of Electro-Optical Engineering, Department of Electronic and Computer Engineering, National Taiwan University of Science and Technology, Taipei, Taiwan
[b] Department of Electrical and Computer Engineering, Institute of Technology and Science, Tokushima University, 2-1 Minami-Josanjima, Tokushima 770-8506, Japan

ARTICLE INFO

Article history:
Received 1 April 2017
Received in revised form 12 September 2017
Accepted 12 September 2017

Keywords:
Ion beam sputtering
Anode layer ion source
Silver oxide
Optical properties

ABSTRACT

An integrated ion beam sputter deposition module utilizing an anode layer ion source has been designed and fabricated. Silver oxide is deposited utilizing this ion beam sputter module. Experimental results show that Ag is fully oxidized only with oxygen partial flow rate equal to and higher than 0.8. With an anode voltage of 700 V, silver oxide with (1 1 1) preferred orientation was obtained. Increasing anode voltage to 1500 V results in (2 0 0) orientated silver oxide thin films. Two band gaps can be identified that increase from 1.0/2.6 eV to 2.0/2.8 eV as anode voltage increases from 700 to 1500 V, respectively. As anode voltage increases, XPS analysis shows that Ag $3d_{5/2}$ core level peak position shifts from 367.3 to 367.7 eV. This confirms that increased kinetic energy of sputtered atoms results in partial reduction of AgO to Ag_2O. Fully oxidized silver oxide samples are likely to be p-type while the resistivity is in the range of 0.7–2.0 $\times 10^4$ Ω·cm.

1. Introduction

Ion beam sputter deposition (IBSD) is a widely used technique in semiconductor thin film deposition [1]. In IBSD, average kinetic energy of sputtered atoms can reach 5–15 eV [2], much higher than that of thermal evaporation which is less than 1 eV. This special property results in improved adherence, hardness and structural stability of the deposited material. IBSD has been commonly used for the deposition of optical thin films [1], indium tin oxide transparent oxide [3,4], ZnO [5–8], $YBa_2Cu_3O_{7-\delta}$ superconducting thin films [9], β-C_3N_4 [10], PTFE [11] and TiO_2 [12]. A common IBSD system includes an ion source and a target holder which may hold multiple targets [6,8]. Common ion sources utilized in IBSD include cold hollow cathode [4], Kaufman-type ion gun [6,9,10] and helicon-wave excited plasma sources [7]. In all arrangements, substrates are positioned in a plasma free position upstream of the sputtering target that condensation of sputtered atoms results in the formation of thin film or nanostructures. Due to the arrangement of a separate ion source, IBSD usually requires larger vacuum chambers and higher manufacturing cost. To minimize the cost, we've developed an ion beam sputter module that integrates an anode layer ion source with the sputtering target. Anode layer ion sources, or hall plasma accelerators, have been widely used as ion thruster engines [13,14] since 1960. Recently anode layer ion source has been utilized in ion beam assisted deposition of GaN [15] that high quality GaN can be deposited at reduced temperature. Our design integrates an anode layer ion source with a 2″ sputtering target that the total volume in the vacuum chamber is less than 350 cm^3. Only a single DC high voltage power supply is needed for the operation of this sputter module.

To demonstrate the feasibility of this sputter module, silver oxide (Ag_xO) thin films were deposited under various processing conditions. Silver oxide is a promising material for high density optical storage, fluorescence imaging and for anti-bacterial applications. However, its band gap, carrier type and resistivity are highly dependent on preparation methods [16–18]. This is mainly due to incomplete oxidation of Ag and the presence of mixed AgO/Ag_2O phases. Weaver et al. [16] demonstrated that annealing of AgO at 300 °C results in reduction of AgO to Ag_2O. Further increasing the annealing temperature to 400 °C results in complete reduction of Ag_2O to Ag. This indicates that oxidation state of silver oxide deposited by IBSD may be dependent on the energy of the sputtering ions. Should the oxidation state of silver oxide can be controlled, it may facilitate the advancement in the development of silver oxide based optoelectronic devices.

* Corresponding author.
E-mail address: lcchao@mail.ntust.edu.tw (L.-C. Chao).

http://dx.doi.org/10.1016/j.nimb.2017.09.011
0168-583X/

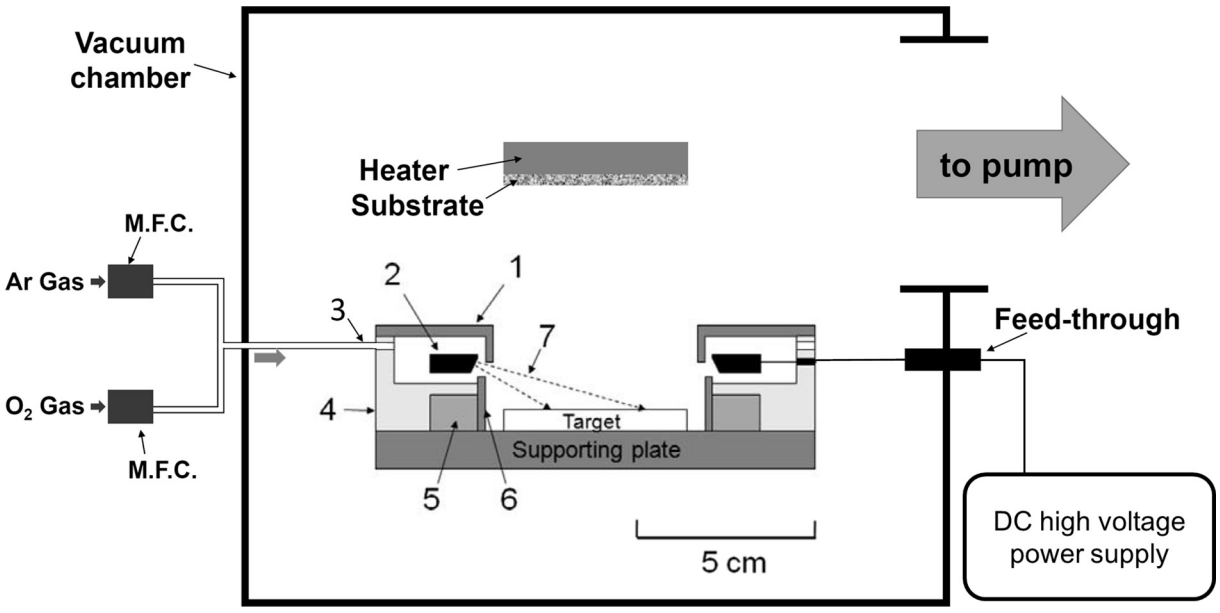

Fig. 1. A schematic drawing of the deposition chamber. In the chamber is a 2″ integrated ion beam sputter module. 1: upper cathode, 2: anode, 3: gas inlet, 4: outer shielding, 5: permanent magnets, 6: lower cathode, 7: ion beam. During deposition, the anode is biased at V_a, while all other components are grounded to earth.

2. Experimental

Fig. 1 shows a schematic drawing of the deposition chamber. Shown in Fig. 1 is a 2″ integrated ion beam sputter module [19]. The ion source is composed of an annular-shaped electrode with its electrode facing the sputtering target. The surface normal of the anode is at ~60° relative to the normal of the sputtering target surface. The anode is surrounded by two annular-shaped cathodes, the upper cathode and the lower cathode. The upper cathode opening diameter is smaller than that of the lower cathode opening diameter, while these two cathodes are offset vertically. This arrangement creates an opening that allows ion beam to go through [19]. Permanent magnets are attached to the cathode to create a magnetic field that is approximately perpendicular to the anode surface normal. As a DC voltage is applied to the anode (V_a), an electric field is formed that is approximately perpendicular to the magnetic field. Due to the Lorentz force, electrons move in a helical trajectory toward the anode and stable plasma is achieved by electron impact ionization.

In an anode layer ion source, the ionization cross-section of working gas atom is dependent on the kinetic energy of electrons [13]. If the working gas is argon, the optimized electron kinetic energy should be between 45 and 110 eV, which implies a hall drift velocity E/B of 2.8×10^6 to 4.4×10^6 m/s [13]. In the present design, the magnetic field at the center of the cathode opening is ~800 G, indicating that the electric field at this location should be between 2.2 and 3.5×10^5 V/m. The electric field of this ion beam sputter module is solved using nine-point finite difference method [20]. Calculation results show that with V_a of 700 and 1500 V, electric field at the center of the cathode opening is 1.4×10^5 and 3.0×10^5 V/m, respectively. Both are close to the optimized values [13] indicating that efficient plasma generation can be achieved with these anode voltage values.

During the deposition of silver oxide, quartz substrates were positioned at 65 mm upstream of the target and a metallic silver target (99.99%) was used. Silver oxide is deposited with V_a = 700 and 1500 V while both oxygen and argon were controlled by separate mass flow controllers (M. F. C.) and were passed simultaneously into the ion source. Five set of samples were deposited

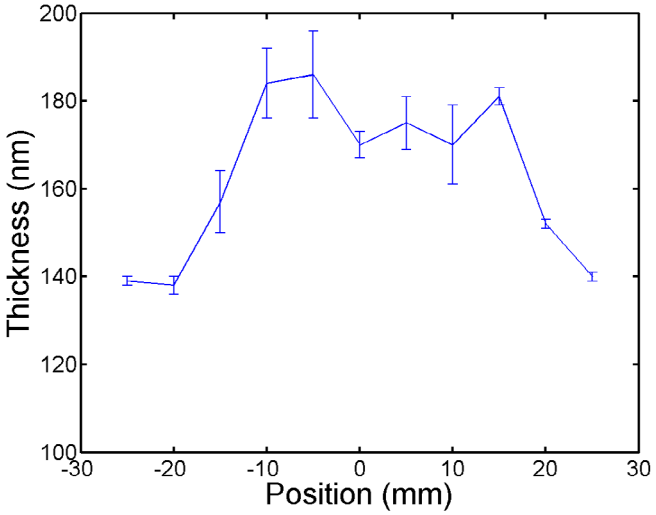

Fig. 2. Position dependent thickness of metallic Ag thin film deposited at room temperature with a V_a = 1000 V and a discharge current of 10 mA.

with Ar flow rates of 4, 3, 2, 1, 0 sccm, while corresponding O_2 flow rates were 1, 2, 3, 4 and 5 sccm, respectively. These results an oxygen partial flow rate O_{pf}, which equals the oxygen flow rate divided by total gas flow rate, from 0.2 to 1.0 while O_{pf} = 1.0 implies oxygen gas only. The deposition chamber was pumped by a diffusion pump with a liquid nitrogen trap and the base pressure was 5×10^{-6} Torr. During the deposition, pressure in the deposition chamber was ~1 mTorr.

Surface morphology of the sample was characterized by a field emission scanning electron microscope (FE-SEM, JEOL JSM −6500F, 15 keV). X-ray diffraction patterns were measured with a Bruker D2 Phaser X-ray diffractometer using Cu Kα, radiation (λ = 0.15406 nm) in the θ-2θ mode. Transmission spectra were collected utilizing a deuterium-halogen light source and a CCD imaging spectrometer. Uniformity test was performed by depositing metallic Ag at room temperature and thickness of the metallic Ag film was characterized by a surface profilometer (Veeco DekTak