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Electrical and optical properties of AlNxOy thin films deposited by reactive DC magnetron sputtering

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Aluminium, Al, is a metallic material used in a large variety of technological fields, such as surface plasmon-coupled emission (SPCE) devices for biochemical applications and it is also a good candidate to be used as nonresonante plasmonic nanoparticle in thin-film silicon solar cells. Aluminium nitride, AlN, is a semiconductor material and it can be used in the fabrication of optical sensors, LEDs, surface/bulk acoustic wave devices and in electronic packaging. Aluminium oxide, Al_2O_3, is an insulator material, used as protective film, as gate dielectric in flash memory circuits, OTFTs, MOSFET, etc. The AlO_y system is also important in solar selective coatings since it exhibits very high solar selectivity. The possibility to associate the overall set of properties of the above mentioned base-materials might be the starting point for a material that may combine specific advantages of each of the three systems, Al, AlN_x and AlO_y, according to the particular requirements of a given application. In fact, the addition of small amounts of oxygen and nitrogen to a growing Al film can give rise to an oxynitride film with a wide range of different properties, where the optical and electrical ones may be tailored between those of the pure aluminium and those of aluminum nitride and oxide. In this work thin films of AlN_xO_y were prepared by reactive DC magnetron sputtering, using a pure Al target and an $Ar/(N_2,O_2)$ gas mixture. Preliminary Transmission Electron Microscopy and EELS analysis suggested the growth of films with Al nanoparticles randomly embedded in an AlN_xO_y matrix. The particular structure, morphology and composition of the films induced a wide variation in the electrical properties, which can be explained using a tunnel barrier conduction mechanism for the electric charge transport through the films, as well as distinct optical responses, such as an unusual large broadband absorption for some films, with potential applications in solar cells and thermal photovoltaics.

Keywords
AlNxOy
Electrical and optical properties

ELECTRICAL AND OPTICAL PROPERTIES of AlN_xO_y THIN FILMS DEPOSITED by REACTIVE DC MAGNETRON SPUTTERING

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In this work a set of films of AlN_xO_y and two sets of the correspondent binary systems, AlN_x and AlO_y, were produced using reactive DC magnetron sputtering, using an aluminium target and an Ar + (N_2 +/or O_2) gas mixture. The discharge characteristics (target potential) and deposition rate, chemical composition, structure, electrical and optical properties of the ternary system were compared to those of the binary systems in order to test whether the oxynitride films have a unique behaviour or are simply a transition between AlN_x and AlO_y.

DEPOSITION TECHNIQUE

DC magnetron sputtering
Target: Aluminium, 99,6 % purity
Substrates: Glass, Silicon <100>
Substrate temperature before plasma: 373 K
Partial pressure of Argon: 0.3 Pa
Reactive gas: N_2; O_2 and N_2+O_2 (17:3)
Rotating substrates: 9 r.p.m.
Bias: GND
Target current density: 75 A.m^{-2}
Discharge parameters monitored by a Data Acquisition/ Switch unit Agilent34970A

DEPOSITION CHARACTERISTICS

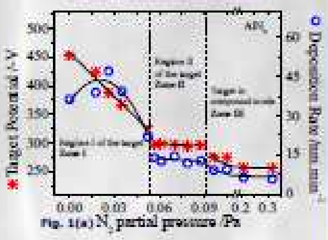

Fig. 1(a) N_2 partial pressure /Pa

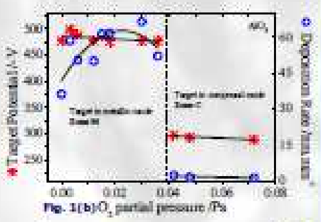

Fig. 1(b) O_2 partial pressure /Pa

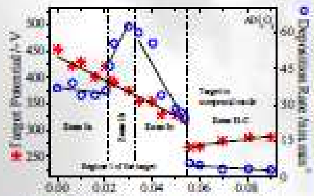

Fig. 1(c) N_2+ O_2 (17:3) partial pressure /Pa

Fig. 1 Target potential and deposition rate of (a) AlN_x, (b) AlO_y and (c) AlN_xO_y systems.
The Target Potential is clearly influenced by the gas mixture partial pressure. In the AlO_y system the transition from a clean to a poisoned target is very abrupt, while in the AlN_x and AlN_xO_y systems the transition is smoother.
The deposition rate (thickness/deposition time) has also distinct variations in each system.

RESULTS AND DISCUSSION

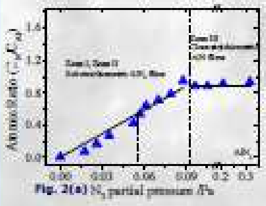

Fig. 2(a) N_2 partial pressure /Pa

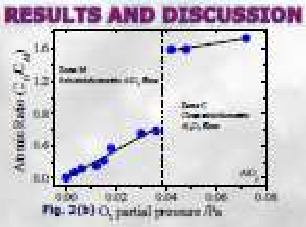

Fig. 2(b) O_2 partial pressure /Pa

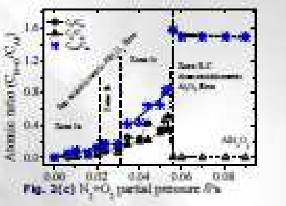

Fig. 2(c) N_2+O_2 partial pressure /Pa

Fig. 2 Atomic ratio of (a) AlN_x, (b) AlO_y and (c) AlN_xO_y films.
The transition from sub-stoichiometric towards close-stoichiometric films is relatively smooth in AlN_x, very abrupt in AlO_y and different tendencies can be found in AlN_xO_y system according to the particular zones identified.

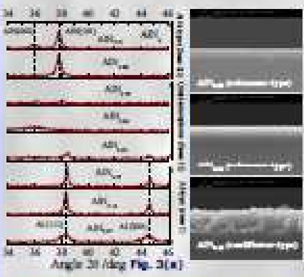

Fig. 3(a)

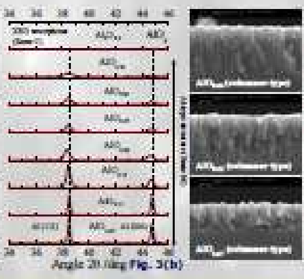

Fig. 3(b)

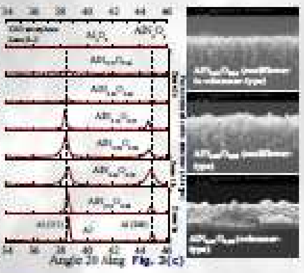

Fig. 3(c)

Fig. 3 XRD and representative SEM cross sections of (a) AlN_x, (b) AlO_y and (c) AlN_xO_y systems.
In the AlN_x system an Al-type structure is observed for low stoichiometries (zone I), then the films become XRD amorphous (zone II) and finally crystallize in a hexagonal (wurzite) structure (AlN-type structure). The sub-stoichiometric AlO_y films (Zone M) are also composed of Al crystals, becoming XRD amorphous when close-stoichiometric Al_2O_3 films are formed (Zone C). In the AlN_xO_y system the Al-type structure is maintained in the sub-stoichiometric films (Zone Ia, Ib), becoming amorphous in zone Ic, ending up completely amorphous in zone II-C (again close-stoichiometric Al_2O_3 films).
A non-columnar growth was found in some films with Al-type structure. These films, with cauliflower-like growth, are porous, which may explain the high deposition rates observed in some films.

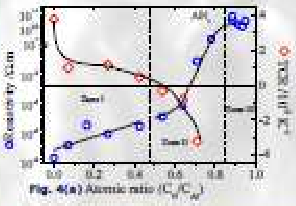

Fig. 4(a) Atomic ratio (C_N/C_{Al})

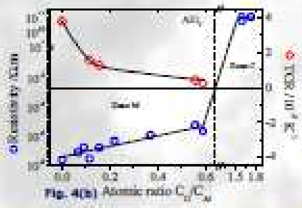

Fig. 4(b) Atomic ratio C_O/C_{Al}

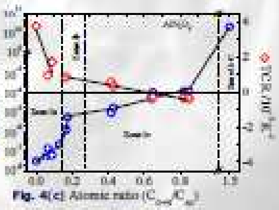

Fig. 4(c) Atomic ratio (C_{O+N}/C_{Al})

Fig. 4 Electrical resistivity and temperature coefficient of resistance (TCR) of (a) AlN_x, (b) AlO_y and (c) AlN_xO_y systems.
The electrical resistivity gradually increases 3-4 orders of magnitude in the films with Al-type structure. It increases further with the rise of the atomic ratio towards semi-conductor and insulator-type resistivities.
The TCR, measured for the high conductive samples, decreases with the increase of the atomic ratio and can even be negative in the systems with nitrogen, AlN_x and AlN_xO_y.

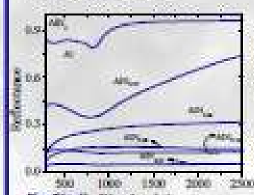

Fig. 5(a-i) Wavelenght/ nm

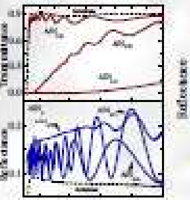

Fig. 5(a-ii) Wavelenght /nm

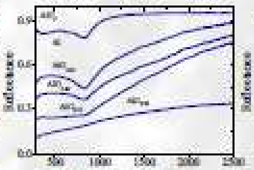

Fig. 5(b) Wavelenght /nm

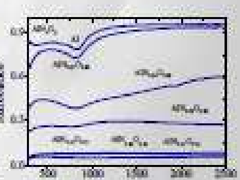

Fig. 5(c) Wavelenght /nm

Fig. 5 Reflectance and transmittance of (a-i and a-ii) AlN_x system and reflectance of (b) AlO_y and (c) AlN_xO_y systems.
The films indexed to zone I of the AlN_x system are opaque and the typical interband absorption of aluminium at ~800 nm can be observed.
The reflectance drops from the typical Al profile towards very low values. In zone II, as the atomic ratio increases, the reflectance increases again and interference fringes can be observed for higher ratios. The films become semi-transparent, ending up with a very high transmittance in zone III. In AlO_y system, the films indexed to zone M are opaque with a marked decrease of the reflectance, becoming transparent in zone C (as expected since the films have Al_2O_3-type compositions). In AlN_xO_y system the reflectance also drops to low values as the atomic ratio increases and also a flat reflectance, as low as 5%, can be observed in the films indexed to zone Ic.

CONCLUSIONS

The composition and structure of the films are strongly dependent of the target condition and deposition characteristics [1]. It was found that the three systems have distinct electrical and optical responses opening the possibility to tailor the properties of the AlN_xO_y from those of the correspondent binary systems, according to the application envisaged. The properties of the ternary system can be explained assuming that the films (zone Ic) are in fact a percolation network of aluminium nanoparticles embedded in an oxide/nitride matrix [2]. The aluminium grains can form irregularly shaped clusters with different sizes through the matrix, inducing a broadband absorption nearly independent of the wavelength. The conductivity is also governed by the constrictions between grains that can be in contact or separated by insulating barriers (oxide/nitride and/or voids). The barrier component of the films resistance has a negative dependence on the temperature and thus explaining the negative TCR for some films.

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[2] J. Borges, N. Martin, N.P. Barradas, E. Alves, D. Eyidi, M.F. Beaufort, J.P. Riviere, F. Vaz, L. Marques, Thin Solid Films 520/21 6709

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