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Fabrication and surface characterization of pulsed reactive closed-field unbalanced magnetron sputtered amorphous silicon nitride films

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Abstract

Amorphous silicon nitride (a-SiN_x) thin films were fabricated by pulsed reactive closed-field unbalanced magnetron sputtering ultra-high purity *n*-type single crystal silicon in Ar–N_2 mixtures. The effect of N_2 fraction on the discharge behavior, deposition rate, composition, chemical bonding configurations, surface morphology, nano-hardness, elastic modulus and optical band gap were primarily investigated. It was found that good stability of reactive sputtering process was maintained by the adoption of the bipolar pulsed magnetron power supply with 180° out-of-phase and the pulsed substrate bias. The arc events and the disappearing anode effect in DC reactive magnetron sputtering of a-SiN_x films were prevented. A higher deposition rate (>20 nm/min) for a-SiN_x films was achieved. The radical transition of the sputtering mode leads to the deposition rate initially decreased dramatically and then slowly with the increase of N_2 fraction. N to Si atomic ratio (N/Si) gradually increased and N is preferentially incorporated in its NSi_3 stoichiometric ratio configuration and the Si–N network followed a tendency to tetrahedral chemical order with the increase of N_2 fraction in the inlet gases. The a-SiN_x films deposited at high N_2 fraction were consistently N-rich. The film surface microstructure was transformed from coarse granular mounds surrounded by tiny micro-void regions to homogeneous, continuous, dense and slender hills, as well as a progressive densification and refinement of the film microstructure occurs as the N_2 fraction is increased. With the increase of the N/Si atomic ratio, the resistance of the a-SiN_x films surface region to plastic deformation improved; hardness and elastic modulus increased, correspondingly. The as-sputtered a-SiN_x films exhibit good optical transparency in visible region and the optical band gap E_{opt} can be varied in a broad range of 1.70–3.62 eV depending on the N_2 fraction in Ar–N_2 mixtures. The increment of optical band gap E_{opt} of the as-sputtered a-SiN_x films is determined primarily by the recession of the valence band maximum.
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Keywords: a-SiN_x thin films; Closed-field unbalanced magnetron sputtering; Pulsed magnetron sputtering; Pulsed substrate bias; Optical band gap; Valence band spectrum

1. Introduction

Amorphous silicon nitride (a-SiN_x) thin films are the subject of great interest not only for their excellent properties such as high chemical inertness, high thermal stability and corrosion resistance, but also for their excellent mechanical, optical and good dielectric properties. SiN_x films are conventionally fabricated by low-pressure chemical vapor deposition (LPCVD) [1,2], plasma enhanced chemical vapor deposition (PECVD) [3,4], reactive evaporation [5], ion beam deposition [6,7] and more recently by reactive sputtering [8–10], etc.

In particular, radio frequency reactive magnetron sputtering is the most popular selected method to synthesize a-SiN_x films by different target materials (Si or Si_3N_4) and sputtering gas species (Ar, N_2 or NH_3), and with negative direct current (DC) substrate bias. However, it should be noted that the serious shortcoming of radio frequency sputtering is its relatively low deposition rate (<10 nm/min) to the DC reactive sputtering, and the expensive experiment apparatus, reported by many authors, is insuffi-

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cient for industrial production of functional films [11–14]. Moreover, when the conventional negative DC substrate bias was applied to deposit dielectric films on highly insulating substrates, the ionic current fluxes would quickly charge up at the surface, reducing the ionic current flux and the energy used to bombard the surface [15,16]. Consequently, the ion energy distribution becomes non-uniform and control of the ion bombardment during film growth becomes difficult [16–18].

Numerous studies have shown that pulsing magnetron discharge at medium frequencies (10–200 kHz), when depositing highly insulating materials, can improve the deposition rate and stabilize the discharge process, and almost eliminate arcing and the disappearing anode effect caused by the accumulation of positive charges which can appear on the surface of dielectric films that grow on the target, substrate and surrounding reactor walls [12,14,19]. Based on our literature research, the study of using pulsed magnetron sputtering on the fabrication of a-SiN_x films was few. And also, very few studies have been done on the application of pulsed bias voltage to the substrate. Therefore, a systematic investigation of pulsed reactive magnetron sputtering and pulsed substrate bias on the deposition of a-SiN_x films and their properties is highly needed.

In this work, a-SiN_x films were deposited on three types of substrates with different conductivity including Si (100), AISI 316L stainless steel and optical glass using bipolar pulsed DC reactive closed-field unbalanced magnetron sputtering system. The effects of N_2 fraction (N_2/(Ar+N_2)%) on the discharge behavior, deposition rate, composition, chemical bonding configurations, surface morphology and microstructure, nano-hardness, Young's modulus and optical band gap were primarily investigated.

2. Experimental details

2.1. Film deposition

The a-SiN_x films were deposited using our newly designed pulsed reactive closed-field unbalanced sputtering apparatus. A schematic diagram of the sputtering device is shown in Fig. 1. It consists of a stainless steel vacuum chamber with diameter of 500 mm, height of 600 mm, four symmetrical planar rectangular magnetron source (170× 134×6 mm^3) and a movable, heated substrate holder which is electrically isolated from the grounded vacuum chamber. Turbo-molecular pumps coupling with a machine pump system were used to evacuate the vacuum chamber. Targets B and D were connected to a SP-5MB bipolar symmetric pulsed-DC power supply using constant-current mode. Ultra high purity n-type single crystal silicon (99.99999%) was used as the target material. The phase difference between targets B and D was 180° and the voltage polarity periodically changes from negative to positive. In such case, the sputtering process takes place from the silicon target during the negative pulse and the discharging process takes place as a result of electron bombardment during the positive pulse, alternately. In all cases, the bipolar pulsed power with 30 kHz pulse frequency and 50% duty cycle were kept. The pulsed bias voltage of −100 V at 70 kHz pulse frequency, 50% duty cycle was also applied to the substrate, concurrently. Target and the substrate were pre-sputtered for 3 min at 0.6 Pa by argon discharge to remove the oxide layer, separately. High purity Ar (99.999%) and N_2 (99.999%) were introduced into the vacuum chamber using two independent mass flow controller and the total flow rate was fixed at 60 sccm. During deposition, the working pressure was monitored around 0.8 Pa by the valve

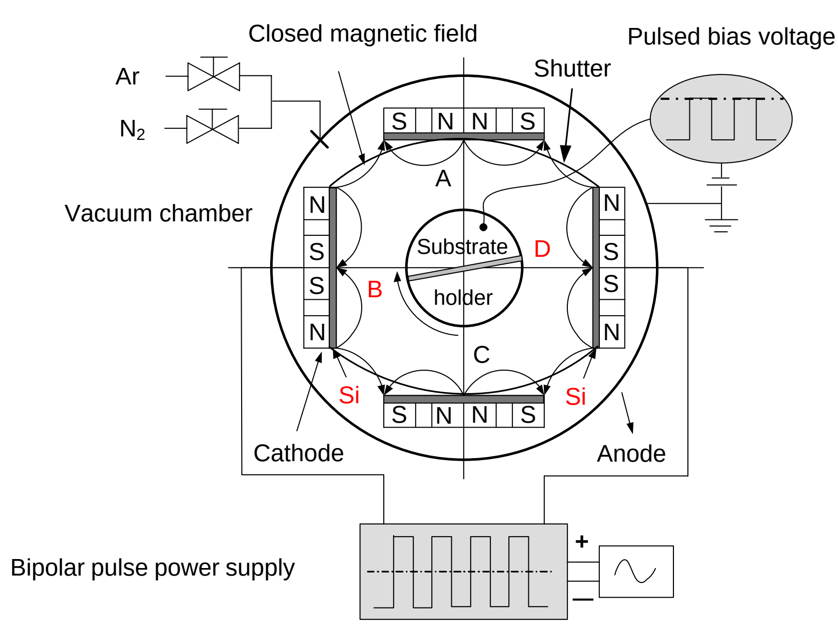

Fig. 1. Schematic diagram of the pulsed reactive closed-field unbalanced sputtering system.

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