Substrate Response During Dual Bipolar Pulsed Magnetron Sputtering

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ABSTRACT

Dual bipolar pulsed magnetron sputtering is a highly successful technique for the deposition of transparent dielectric materials. Operating in the mid-frequency range (100-350 kHz), the periodic target voltage reversals suppress arcing and stabilize the reactive sputtering process. Asymmetric bipolar pulsed DC power supplies are commonly used to drive this process. For simplicity these supplies are normally assumed to display "square wave" characteristics. However, as pulse frequencies are increased, particularly to in excess of 150 kHz, target voltage waveforms increasingly depart from this idealized behavior. Very significant voltage overshoots are observed in each direction during each half of the pulse cycle. Monitoring of the substrate I-V waveforms during operation has revealed that similar transient "spikes" also occur here. Complementary Langmuir probe studies have shown increased plasma heating as pulse frequency is increased and mass spectrometry studies have confirmed the existence of ions whose energy is dependent on the pulsing characteristics at the target. As a result, there will be short bursts of high energy ions incident at the substrate during pulsed sputtering. Furthermore, the energy and flux of these ions appear to be frequency dependent. Clearly, such bursts of high energy bombardment could have a significant influence on the growing film. Consequently, investigations into the complex processes involved during bipolar pulsed sputtering are being carried out. Particular attention is paid in this paper to the frequency dependence of structural and optical properties of alumina and titania films grown via this technique.

INTRODUCTION

Pulsed magnetron sputtering has transformed the deposition of transparent dielectric coatings. Many studies have shown that pulsing the magnetron discharge in the mid-frequency range (20-350 kHz) can suppress arcing at the target and stabilize the deposition process [1-4]. As a consequence, high quality defect-free coatings can be produced at commercially useful rates.

The market sectors for high quality transparent functional films are growing rapidly. There are many diverse applications including low emissivity and solar control coatings, anti-reflective coatings, barrier layers for packaging, opto-electronic devices, display panels and security devices [3,5-6]. In all cases, high rate stable deposition conditions are required for economic viability.

In single magnetron systems, during the long term deposition of dielectric materials, all surfaces eventually become coated with an insulating layer. Thus, anode surfaces are progressively lost, leading to significant variations in deposition conditions with time [3]. The dual bipolar process overcomes this problem by connecting two magnetrons to the same alternating power supply. The magnetrons are pulsed 180° out of phase to each other, such that each acts alternately as a cathode and an anode. Consequently, clean anode surfaces are always available and long term (>300 hours) process stability can be achieved [5]. As a result, the dual bipolar process has become the process of choice for many of the applications referred to earlier.

Despite the success of the dual bipolar process, there are many aspects of this complex process that are not yet well understood, particularly the interrelationships between target voltage waveforms and plasma parameters and their impact on film growth. For example, asymmetric bipolar pulsed DC power supplies are commonly used to drive this process [3,4], and for simplicity these supplies are normally assumed to display "square wave" characteristics. However, as pulse frequencies are increased, particularly to in excess of 150 kHz, target voltage waveforms increasingly depart from this idealized behavior. Very significant voltage overshoots are observed in each direction during each half of the pulse cycle, the magnitude of which increase with increasing pulse frequency [7]. Monitoring of the substrate I-V waveforms during operation has revealed that similar transient "spikes" also occur here [7]. Complementary time averaged [8] and time resolved Langmuir probe studies [9] have shown that parameters such as plasma density and electron temperature all increase with increasing pulse frequency. Additionally, mass spectrometry studies of the distribution of ion energies at the substrate in an asymmetric bi-polar pulsed DC magnetron discharge [10] have confirmed the existence of populations of ions whose energies can be directly related to distinct phases, or features within the target voltage waveform. In particular, high (>100 eV) energy ions are created as a result of the positive voltage overshoot at the beginning of each pulse off

cycle. As a result, there is a short burst (<□1μs) of high energy ions incident at the substrate during each pulse cycle. Clearly, such bursts of high energy bombardment could have a significant influence on the growing film. Furthermore, the energy and flux of these ions appear to be frequency dependent. Detailed investigations are, therefore, underway at Salford and UMIST to elucidate the relationships mentioned above. Time-averaged and time-resolved Langmuir probe studies [8,9] and mass spectrometry studies [10] have been reported elsewhere. This paper considers the effect of pulse frequency on the structure and properties of alumina and titania films grown by dual bipolar pulsed sputtering in a closed field unbalanced magnetron sputtering (CFUBMS) system.

EXPERIMENTAL

The experiments reported here were all performed in a Teer Coatings Ltd. UDP450 CFUBMS system, which has been described in detail elsewhere [4]. Two 300 mm x 100 mm Gencoa VTech variable magnetrons were installed in the vertically opposed configuration. A central rotating substrate holder was also installed, with the substrate-to-target separation set at 110 mm. The magnetrons were driven by a dual channel Advanced Energy® Pinnacle Plus™ asymmetric bipolar pulsed DC power supply. In dual cathode mode, this unit allows the magnetrons to be driven at pulse frequencies in the range 100 to 350 kHz, at a duty factor of 0.5. In the pulse-off period the reverse voltage is nominally set to 10% of the pulse-on voltage.

Alumina and titania films were deposited by the dual bipolar pulsed reactive sputtering of pure (99.5%) metal targets in Ar/O_2 environments. Films were deposited at pulse frequencies in the range 100 to 350 kHz. The reactive sputtering process was controlled in the partially poisoned mode using the optical emissions monitoring (OEM) technique. Deposition conditions were chosen, on the basis of previous studies [4], that were expected to produce stoichiometric Al_2O_3 and TiO_2 film compositions. In all cases, the target currents were fixed at 4 A and the argon partial pressure at 1.25 mTorr. Run times were varied to produce batches of "thick" and "thin" coatings with thicknesses of approximately 2 μm and 500 nm, for alumina, and 800 nm and 250 nm for titania. The coatings were deposited onto green plate float glass, which had been pre-cleaned using rouge paste (a mixture of ceria and alumina powders), acetone and IPA. No plasma pre-cleaning of the substrates was carried out.

The structure and composition of the coatings were determined by scanning electron microscopy (SEM Cambridge Stereoscan 600), electron probe microanalysis (EPMA JEOL JXA 50A, equipped with WDAX), X-ray diffraction (XRDD Siemens D5000, with Cu Kα source, operating in θ-2θ mode) and Rutherford Backscattering (RBS 2 MeV He ion beam).

Hardness measurements of the alumina films were made using a Fischerscope H100 microhardness tester (Vickers indentor), and a Micro Materials Nanotest 500 nanoindentor was used for the titania films. Single pass scratch testing was performed using a Teer Coatings Ltd. ST3001 Tribotester, equipped with an acoustic emission detector and image analysis facilities. Surface roughness was measured using a Veeco Dektak^3 ST. All of the above analyses, or measurements were performed on the "thick" batches of films. Finally, the optical properties of the coatings were determined using Aquila Instruments nkd6000 and Perkin Elmer λ900 spectrophotometers, with additional measurements carried out using a Sentech SE800 spectroscopic ellipsometer. These measurements were generally performed on the "thin" batches of films, although some "thick" titania films were also analyzed for comparative purposes.

Finally, in a series of additional experiments, substrate temperatures were measured using a mineral insulated thermocouple attached to the front face of the substrate holder. The thermocouple readout was recorded after fixed run times of 45 minutes for the reactive sputtering of titania at various pulse frequencies. Since the thermocouple was clamped to the substrate holder, the holder could not be rotated during these experiments.

RESULTS

Structures and compositions

The most immediately striking effect of pulsing the discharge during the reactive sputtering of alumina is the suppression of arcs at the target. This has a very significant impact on the structure of coatings grown using this technique [2]. In these experiments, under SEM examination, all the alumina films appeared to be fully dense, defect free structures. Indeed, no variation in structure with pulse frequency was observed. Figure 1 shows a typical example, in this case grown at a pulse frequency of 150 kHz. By way of comparison, Figure 2 shows the structure of an alumina film grown by DC reactive sputtering under otherwise identical conditions. In the DC case, arcing occurred throughout the deposition process and, as a result, the coating contains many defects. EPMA and RBS analysis confirmed that all the pulsed alumina films had a stoichiometric Al_2O_3 composition, whilst XRD analysis showed that these coatings were amorphous.

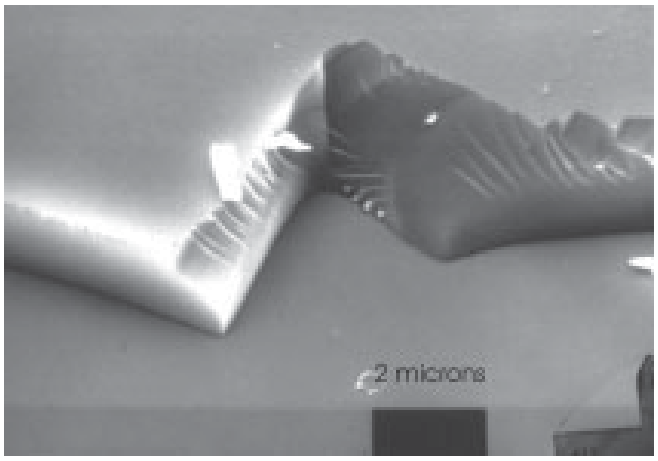

Figure 1: SEM micrograph of fracture section of alumina film deposited by pulsed DC reactive dual magnetron sputtering (150 kHz pulse frequency).

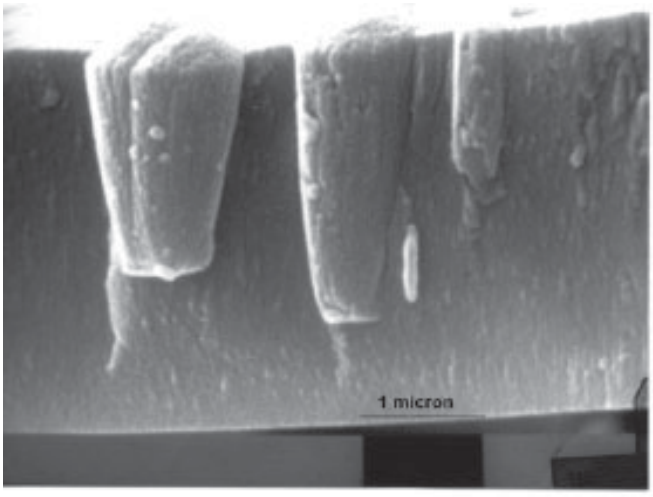

Figure 2: SEM micrograph of fracture section of alumina film deposited by DC reactive dual magnetron sputtering.

Titania films also showed no discernible structural or compositional (all were stoichiometric TiO_2) variations with frequency. In this case, though, the structures could best be described as dense columnar in nature, with a "rippled" surface. Randomly distributed small dome-topped columns, or nodules, are also evident. Figure 3 shows the surface of a typical pulsed titania film. Arcing is not a problem during the short term (~1 hour) deposition of titania. Thus, the very marked differences in structure between DC and pulsed DC for the alumina films are not apparent here. The DC titania films do, though, show the presence of deep pits in a generally smooth background surface. A typical example is shown in Figure 4.

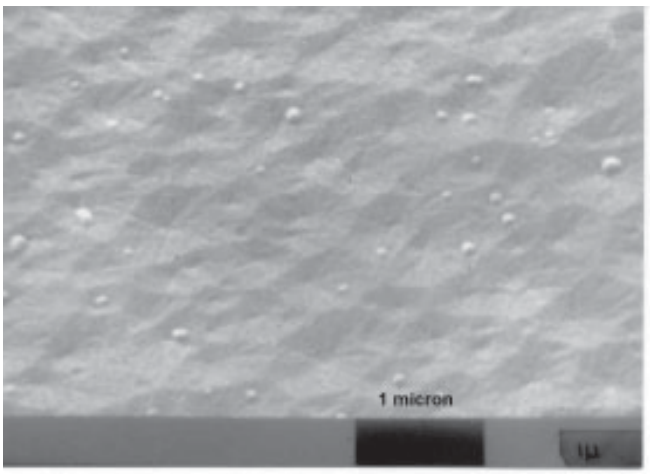

Figure 3: SEM micrograph showing surface features of a titania film deposited by pulsed DC reactive dual magnetron sputtering (pulse frequency =)

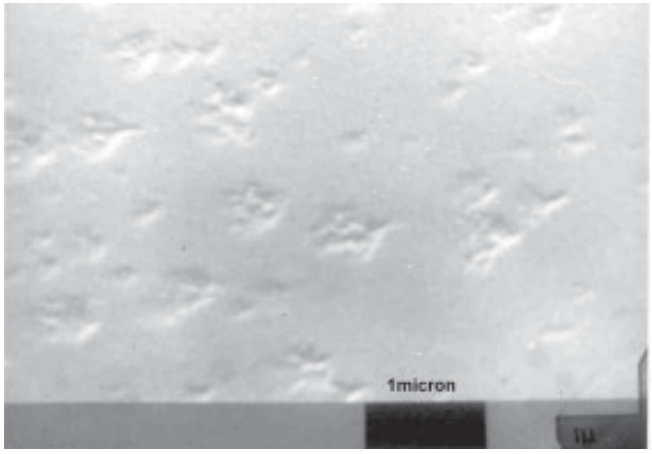

Figure 4: SEM micrograph showing surface features of a titania film deposited by DC reactive dual magnetron sputtering.

XRD analysis showed that all the titania coatings, including the DC films, had rutile structures with strong (110) textures. Figure 5 shows the θ-2θ XRD traces of titania coatings grown by DC and at pulse frequencies of 100, 200 and 350 kHz

Substrate temperature

A general increase in substrate temperatures was observed with increasing pulse frequency. At a frequency of 100 kHz, the temperature recorded after 45 minutes was 55°C, whereas at 350 kHz, the substrate reached 140°C over the same time period. The temperature attained during DC sputtering was 122°C, which was approximately equivalent to pulsing at 225 kHz at a duty of 50%.

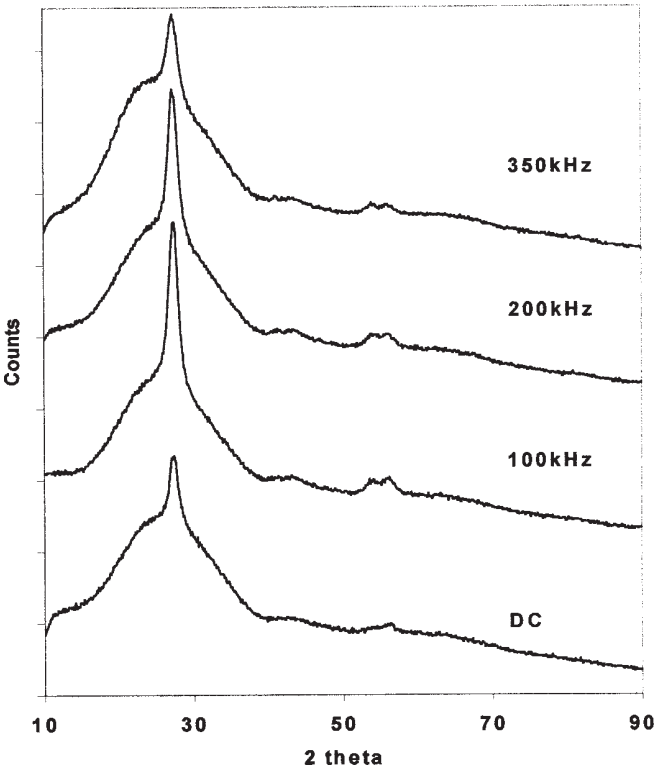

Figure 5: θ-2θ XRD traces of titania films deposited by DC reactive sputtering and pulsed DC reactive sputtering at 100, 200 and 350 kHz pulse frequencies.

Hardness, surface roughness and scratch adhesion

Microhardness measurements were carried out on the alumina coatings using the Fischerscope H100 and nanohardness measurements were made of the titania coatings using the Nanotest 500. In all cases, indentation depths were restricted to 10% of the coating thickness. For both coating materials, no statistically significant variation in hardness was observed with pulse frequency. Hardness values ranged from 12 to 14 GPa for the alumina films, and 11 to 16 GPa for the titania films. The greater spread of values for the titania films could be a function both of the technique used and the greater surface roughness of the films, themselves.

The alumina films showed little variation in surface roughness with pulse frequency. All were extremely smooth with R_a values of the order of 0.5-0.8 nm (i.e., the same order of magnitude as the glass substrates). Although films produced at 350 kHz consistently showed R_a values approximately double this range. It is worth noting that DC alumina coatings, such as the one shown in Figure 2, were found to have R_a values in the range 250-300 nm, i.e., some 500 times rougher than the pulsed DC films.

As would be expected from a comparison of the SEM micrographs, the titania films were found to have rougher surfaces than the alumina films, with R_a values of 4 nm, on average. Again, no statistically significant variation was observed in R_a value with frequency. The surface roughness of the DC titania films, which had R_a values in the range 5 to 10 nm, was certainly influenced by the deep pits present in their surfaces (as shown in Figure 4).

Scratch adhesion testing of the alumina coatings gave critical loads generally in the range 35 to 40 N for adhesive failure, with no apparent trend with frequency. It was noted, though that films deposited at 350 kHz did not fail during testing, implying that their critical loads must be in excess of 40 N, as this was the maximum load applied. This compares very favorably with the average critical load of 14 N obtained for equivalent DC films.

A greater spread of results was observed for the titania films, with critical loads varying from 20 to 33 N, but with no trend with frequency. Results obtained for DC films were at the lower end of this range. Again, though, coatings deposited at 350 kHz did not fail at the maximum applied load of 40 N.

Optical properties

The green plate float glass used as substrates in these experiments is not an ideal material, as, in general, its properties are not well controlled. Nevertheless, useful measurements of transmission and reflection were made, and subsequently used, to calculate refractive index values and extinction coefficients for these films.

For the alumina coatings, maximum transmission was found to be 92% (λ900), or 85% (nkd6000), depending on which spectrophotometer was used. Films grown at pulse frequencies below 250 kHz showed no variation in optical properties. For example, the refractive indices at 550 nm for films grown at 150, 200 and 250 kHz were found to be 1.62, 1.62 and 1.63, respectively. Analysis using a Sentech SE800 ellipsometer on the sample produced at 150 kHz gave a refractive index of 1.67 (550 nm). Extinction coefficients of 1E-04, or lower were calculated for these films.

However, for films grown at frequencies greater than 250 kHz, some variation in optical properties with frequency was observed. The refractive indices at 550 nm for films produced at 300 kHz were 1.65, as measured by spectrophotometry. These coatings were also found to have surprisingly high absorption for alumina ($k=2x10^{-4}$). The reason for this is not clear at this time, although RBS analysis showed no evidence of contamination in the films. At 350 kHz pulse frequency, the refractive indices of the films (550 nm) were found to increase significantly to near bulk values of 1.72, 1.70 and 1.75, as measured using the nkd6000, λ900 and SE800 ellipsometer, respectively. Again, these films showed high absorption ($k=4x10^{-4}$), though no evidence of contamination was found. The refractive index and extinction coefficient data for these

films are summarized in Figure 6. No meaningful optical data could be obtained from the DC alumina films.

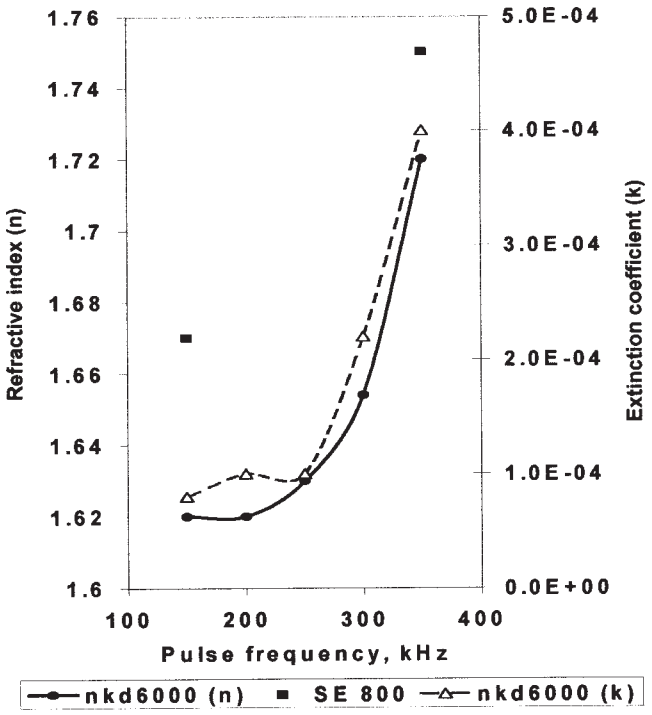

Figure 6: The variation in refractive index and extinction coefficient with pulse frequency for dual bipolar alumina films.

A complete study of the titania films has not yet been completed. However, the maximum transmission for those films tested to date was found to vary from 85% to 90% (nkd6000) without a substrate standard in the reference beam. Refractive indices (550 nm) and extinction coefficients for a DC film and films grown at 100, 200 and 350 kHz are shown in Figure 7. As can be seen, there are indications of a slow rise in n with frequency, but more data are required to confirm this.

DISCUSSION

The results presented here give an indication of the influence of pulse frequency on the structure and properties of alumina and titania films grown by dual bipolar pulsed DC reactive sputtering. Although studies are still continuing, a number of findings can be reported. Firstly, as expected, major improvements in certain properties were observed when comparing films produced by pulsed processing with those produced by continuous processing. This was particularly found to be the case for alumina films in terms of structure, defect density, surface roughness, coating adhesion and optical properties. These very significant differences in properties are attributed largely to the suppression of arcing, and consequent stability of process. Variations in the titania films, when comparing continuous with pulsed films, were less marked. The lesser apparent impact of pulsing in this case might be expected, since, as stated earlier, arcing during the reactive sputtering of titania is not a problem on the same scale as that encountered with alumina, at least during the short depositions performed here.

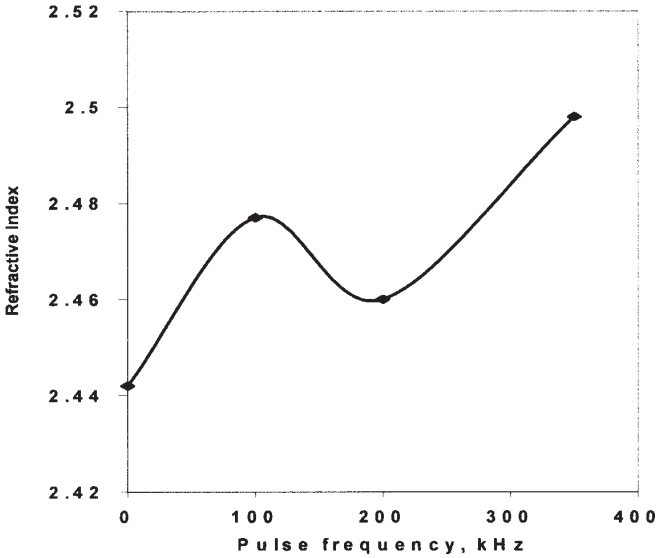

Figure 7: The variation in refractive index with pulse frequency for dual bipolar titania films.

However, beyond the improvements observed as a result of pulsing the magnetron discharges, it is interesting to note that film properties, in general, remained insensitive to pulse frequency (no comment can be made about the possible effect of duty, as this remains constant at 50% during the dual bipolar process). No statistically significant variations were observed in surface roughness, hardness, crystallinity, texture, or critical load. Although in the latter case an, as yet, unaccounted for improvement was observed at pulse frequencies of 350 kHz. The only area in which a notable trend with frequency was observed was in the optical properties of the alumina films (noting again that analysis of the titania films is still ongoing). An increase from 1.62 to 1.72 (or 1.67 to 1.75 by ellipsometry) in the refractive index at 550 nm was recorded as pulse frequency was increased from 150 to 350 kHz.

The lack of impact of pulse frequency on structural and physical properties was somewhat surprising. Time-averaged [8] and time-resolved [9] Langmuir probe studies and mass spectroscopy studies [10] have all shown frequency dependent increases in parameters that control the energy delivered to the growing film. In the latter case, high energy (>100 eV) ions generated during the positive voltage overshoot at the beginning of the pulse off period have been detected at the substrate position. At 100 kHz this flux of ions only contributes a few percent of the total ion energy deposited at the substrate, but at 350 kHz, the contribution rises to an estimated

28% (these studies are on-going). Time-averaged probe studies found that plasma density and electron temperature increase with frequency. Time-resolved studies support this, showing that the total ion power flux to the substrate increases with frequency. Additionally, these studies showed the existence of large (up to 8 times the time-averaged value) instantaneous power fluxes at the initiation of the pulse on period. One response to these variations with frequency was a significant increase in substrate temperature over the range tested. Although it was only at frequencies above 225 kHz that the temperature exceeded that attained during DC sputtering, this may give some indication of the relative impact of the increase in plasma parameters, compared to the decrease in the arrival rate of condensing coating atoms when operating at 50% duty.

Overall, therefore, although plasma parameters may vary significantly with pulse frequency, the substrate response during dual bipolar pulsed sputtering is limited. The frequency dependence of film properties deposited using this process appears to be restricted to relatively subtle parameters, such as refractive index, with other properties remaining largely insensitive to pulse frequency.

CONCLUSIONS

Alumina and titania films have been deposited by dual bipolar pulsed sputtering at pulse frequencies in the range 100-350 kHz (duty = 50%). Compared with DC films, significant improvements were observed in the structures and properties of the pulsed films, particularly the alumina films. This was mainly attributed to the suppression of arc events at the target during pulsed sputtering. Beyond this improvement, though, most properties proved insensitive to pulse frequency. The exception to this was the optical properties of the films, again, particularly the alumina films. In this case, an increase from 1.62 to 1.72 (or 1.67 to 1.75 by ellipsometry) in the refractive index at 550 nm was recorded as pulse frequency was increased from 150 to 350 kHz.

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