THE EFFECT OF HYDROGEN IN DC AND RF SPUTTERING

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Annotation

Sputtering is an important technology used in the fabrication of electronic devices, though it presents some challenges for practical applications. Sputtering targets can become contaminated with the processing gases or substrates. When the sputtering process involves low-reactivity gases, these contaminants can dominate, making it difficult to achieve high-quality films. The sources of contamination vary, but oxygen is the most significant. To minimize the effects of contaminants, hydrogen gas was introduced during sputtering growth. The main hypothesis was that the hydrogen gas would react with oxygen, reducing the oxygen density

in the vacuum chamber. Films were grown using either RF or DC sputtering with metal targets: zinc oxynitride (ZnON) was grown with RF sputtering, and titanium nitride (TiN) was grown with dc sputtering. Energy dispersive spectroscopy (EDS) and x-ray diffraction (XRD) results indicated that film quality significantly improved with the addition of hydrogen.

1. Hydrogen in RF Sputtering

ZnON has attracted the attention for the development of display devices, where high mobility thin-film transistors are required for high speed data manipulation [1]. Nitrogen incorporation into ZnON film is affected by many factors, such as background oxygen contamination. Sputtering chambers may have oxygen contamination originated from previous oxide growths or exposure to air. Introducing hydrogen gas during sputtering growth could potentially address this problem, as a large portion of the ionized oxygen would react with the hydrogen, thereby decreasing oxygen density in the vacuum. The function of hydrogen during sputtering has been investigated before [2-4]. In ref. 2, ArH^+ energy distributions showed a large high-energy tail, which increased the sputtering rate. In ref. 3, it was explained that hydrogen converted the insulating surface of the metal target into a conductive surface, which could increase metal emission from the target.

One important complication in reactive sputtering is change in the target surface condition or target contamination [5,6]. When gases react with the metallic target, the target surface can become covered with oxide or nitride. This results in a decreased emission of metal from the target. The formation of the cover on the target surface can be prevented by using low flows of reacting gases. Another method to prevent the target contamination is gas pulsing. In case of sputtering using nitrogen gas and Zn metal target, Ar gas supply is always on, and N_2 supply is switched between on and off. When N_2 gas is off, the nitrogen-Zn compound on the target surface would be etched away by the Ar ions.

1.1 Details of RF Sputtering

Our sputtering system (SCIEN Tech, Korea) has a 2-inch diameter Zn metal target, with a 13.56 MHz rf power source. Target-substrate distance was 9 cm, and rf power during growth was set at 60 W. High vacuum was achieved by a diffusion pump. The pressure during growth was 3 mTorr at 5-sccm Ar, 1.5-sccm N_2, and 2-sccm H_2 flows. Growth parameters for three samples are listed in Table 1. Ar (5 sccm) and H_2 flows were kept constant. N_2 flow (1.5 sccm) was turned on for 30 sec, and remained off for 90 sec. Eight periods were grown, and total growth time was 16 min. Film thickness' were measured by a Tencor profiler. X-ray diffractions (XRD) were measured by a diffractometer (Rigaku Ultima III), using Cu Kα line as a source. Energy dispersive spectroscopy (EDS) was measured by a scanning electron microscope (JEOL JSM-6380).

1.2 EDS and XRD Results

Table 1. Gas flows, N, Zn, O concentrations of samples A, B, and C.

Sample Name	H_2 flow (sccm)	Growth temp.	N (%)	Zn (%)	O (%)	Thickness (μm)
A	2	RT	2.7	37.6	59.7	0.20
B	2	200°C	2.7	43.1	54.2	0.32
C	0	RT	0.0	24.5	75.5	0.13

RT= Room Temperature

Table 1 shows compositions of N, Zn, and O measured by EDS. Samples A and B show N concentrations of 2.7 % as a result of the additional H_2, while Sample C does not show any N. O concentrations in the table are not accurate, because the measured values contain those from the 150-nm thick SiO_2 layer used in our substrates. Although O concentrations have contribution from the SiO_2 layer, they still show that the H_2 decreased O concentrations in the films. Note that in Table 1, the sample grown at 200°C (sample B) shows larger film thickness. This can be explained as higher reaction rate at the higher temperature.

Figure 1 shows XRD measured in samples A, B, and C. Samples A and B were grown with additional H_2. Data of sample C was magnified by a factor of 5. Although oxygen was not supplied during the growth, all samples show strong ZnO peaks (a: 31.8° (100), b: 34.4° (002), c:

36.4^o (101)). We think that the oxygen was originated from O_2 adsorbed on the chamber wall and the target surface. Samples A and B show strong Zn peaks (d: 39.0^o (100), e: 43.3^o (101)), which is the result of reduction by the additional H_2. ZnN peaks were not observed, and this could be due to low N concentration as shown below. The peaks of samples A and B are stronger that those of sample C, and this indicates that the additional H_2 is also helpful for the growth rate.

2. Hydrogen in DC Sputtering

Titanium nitride (TiN) is an extremely hard material with high electrical conductivity. In very large scale integration (VLSI) circuits, TiN has been used in many applications as a diffusion barrier, adhesion layer, and electrode. Recently, TiN has received attention as an electrode for use in rechargeable batteries. TiN can be deposited in various ways, including dc sputtering [7,8]. For industry applications, dc sputtering is a good method due to its low cost. This method can deposit films of high purity and uniformity on various substrates. TiN is also a good material for discrete electronic devices. However, the use of TiN as a discrete device poses additional problems compared to VLSI application due to its method of manufacturing.

TiN for discrete devices is usually grown on ceramic substrates, since the insulating property of the ceramic substrate is highly desirable for device isolation. The ceramic substrate is made of porous material such as Al_2O_3 powder, which is a strong absorber of O_2 and H_2O. These absorbed gases can degrade the quality of TiN films during sputtering growth. One important complication in reactive sputtering is change in the target surface condition, or target contamination [9]. When gases react with the metallic Ti target, the target surface can become covered with oxide or nitride. This results in a decreased flow of Ti from the target.

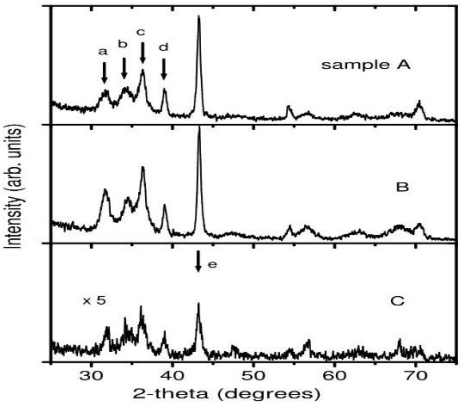


Fig. 1 XRD results measured in samples A, B, and C. Samples A and B were grown with additional H_2, and sample C grown without H_2. Peaks a, b, c are ZnO peaks, and peaks d, e are Zn peaks.

2.1 Methods of DC Sputtering

Ceramic rods (Dong Guan Feng Li Electronics, China) made of Al_2O_3 powder were preheated in vacuum at 400^{O}C before sputtering growth. A rotating barrel was utilized to deposit TiN on ceramic rods placed at the bottom of the barrel. Ceramic rods were cylindrical in shape, with a diameter of 1.7-mm and length of 5.5-mm. The rotation of the barrel caused mixing of the ceramic rods, and the TiN film was uniformly deposited onto the cylindrical surfaces of the rods. 300 grams of ceramic rods were used for one growth. The distance between the target and ceramic holder was 12 cm.

For x-ray diffraction (XRD) and energy dispersive spectroscopy (EDS) measurements, glass or sapphire substrates were used to grow TiN films. Growth time was 30 minutes for glass and sapphire substrates, and 2 hours for ceramic rods. There was no intentional heat supplied, but after a 2-hour growth, the barrel temperature rose to 120^{O}C. A rectangular Ti metal plate (45 cm x 15 cm) was used as the target (THIFINE, Korea). A cryopump (Genesis Vacuum Technology, Korea) was used to pump the chamber. The chamber was initially pumped to 10^{-3} Pa, and Ar and H_2 gases were subsequently introduced. After plasma became stabilized, N_2 gas was introduced. The pressure during growth was 0.3 Pa. Constant power of 1800 W was supplied for dc sputtering.

The target voltage during growth was -480 V with current of ~3 A. XRD was measured by a diffractometer (Rigaku Ultima III), using Cu Kα line as a source. EDS was measured by a scanning electron microscope (JEOL JSM-6380).

2.2 EDS and XRD Results

Initial growth without H_2 produced black or gray TiN films instead of gold colored TiN. The grown films showed high resistance, and XRD data did not show strong peaks. EDS results showed a high nitrogen concentration, with Ti : N ratio of approximately 20 : 80. These results suggested that the target surface was heavily coated with impurities, and that Ti emission from the target was very small.

Next, three different gas flows were used for the growth of subsequent samples (Table 2). Sample F was grown without H_2, and a small flow of N_2 was used. For samples D and E, H_2 was added during growth. For all samples, Ar flow was fixed at 22 sccm. For EDS and XRD measurements, TiN was grown on glass or sapphire wafers for 30 minutes. For growth on ceramic rods, the same gas flows were used with growth time of 2 hours. Ti/N ratios were measured by EDS (Table 2). TiN thickness was measured by a profiler from TiN films grown on glass for 30 minutes. As the ceramic rods were of a cylindrical shape, rod resistance was defined as the resistance measured between the two ends of a cylinder.

Table 2. Gas flows, Ti/N ratios, and rod resistances of samples A, B, and C.

Sample Name	N_2 (sccm)	H_2 (sccm)	Ti (%)	N (%)	thickness (μm)	rod R (Ω)
D	8	8	45.5	54.5	0.83	18
E	11	8	28.1	71.9	0.55	50
F	1	0	26.8	73.2	0.43	9k

Samples D and E had the gold color of TiN, and Sample F was gray in color, Sample F showed a high N concentration, and rod resistance was very large. Note that sample D had the highest concentration of Ti. N_2 flow for sample E was larger than that of sample D, and the N concentration was significantly increased. An increase in the flow of N_2 was related to the increase of N concentration in sample E.

XRD was measured in the three samples (Figure 2). The lowest curve (sample F) is XRD of TiN grown without H_2. Samples D and E were grown with H_2, and XRD data show strong peaks in these samples. Although Ti concentration in sample D was similar to that of sample E, rod resistance of D was much smaller, and strong XRD peaks are shown. These data suggest that the enhanced resistance characteristics of samples D and E are related to the H_2 added during sputtering growth. The XRD peak positions from JCPDS 38-1420 are 36.662^O (111), 42.596^O (200), 61.812^O (220), and 74.068^O (311).

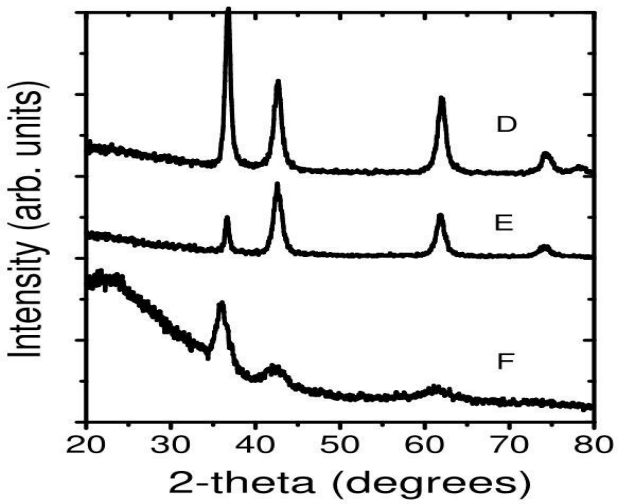


Figure 2. X-ray diffraction (XRD) measured in samples D, E, and F, grown on glass substrates. The four peaks are 36.8^O (111), 42.7^O (200), 61.9^O (220), and 74.5^O (311). Samples

D and E were grown with H_2 added, and sample F was grown without H_2, y-axis scale is the same, and zeros are shifted for clarity.

These experimental results showed that the introduction of hydrogen significantly improved the film quality, as indicated by a lower resistance and strong XRD peaks. The exact mechanism of hydrogen function is unclear at this moment. One possible explanation for this phenomenon may be hydrogen-induced cracking in titanium (hydrogen embrittlement). When metal is exposed to hydrogen gas at ~300^{O}C, metal hydride is formed at the surface, and metal becomes brittle. Hydride formation is an exothermic process, and it can develop rapidly under certain conditions. For example, the presence of energetic ions during sputtering growth can accelerate hydride formation. When metal target has hydride on the surface, metal emission would increase, because dissociation from the target would be easier. Another possible explanation is that lower oxygen density would decrease the mid-course reaction.

The high N concentration in TiN films grown without hydrogen needs more investigation. Although EDS showed a high N/Ti ratio, it does not necessarily mean that the target was coated with nitride. The target could also be covered with a thin layer of oxide. After growth, the target color was metallic, without any irregular patterns. Detailed analysis of the target surface will be needed.

3. Conclusions

We showed that adding hydrogen gas during sputtering growth increased nitrogen concentrations in ZnON films. EDS results showed increased N concentrations and decreased O concentrations by the hydrogen. XRD data showed strong Zn and ZnO peaks. It appears that there is significant amount of oxygen contamination in our growth chamber, which could be the result of O_2 adsorption on the chamber wall. It is not clear at this point how the additional hydrogen contributed during sputtering growth. Decrease of oxygen density is one factor, but there are other possibilities. Increased energy profile of argon ions, target surface modification by the hydrogen, or formation of nitrogen-hydrogen bonding can also occur. This study also showed that adding hydrogen during sputtering growth improves TiN quality. Since TiN in this study was grown on ceramic rods, this growth environment is different from an ideal condition. The hydrogen neutralized the effect of trapped gases, and high quality was confirmed by x-ray diffraction and energy dispersive spectroscopy. These results showed that TiN could be grown on ceramic substrates for discrete device applications.

References

1. J. Choi, W. Jeon, J. Mun, and J. Jo, ‘Hydrogen-assisted Nitrogen Incorporation in zinc oxynitride films grown by rf sputtering,’ Electronics Letters, vol. 57, pp. 292-293, 2021.

2. E. Lee, A. Benayad, T. Shin, H. Lee, D. Ko, T. S. Kim, et al.: ‘Nanocrystalline ZnON; ‘High mobility and low band gap semiconductor material for high performance switch transistor and image sensor application’, Sci. Rep., 4, Article ID 4948, 2014.

3. J. Park, H. Jeong, H. Lee, H. Nahm, J. Park, ‘The resonant interaction between anions or vacancies in ZnON semiconductors and their effects on thin film device properties’, Sci. Rep. 7, Article ID 2111, 2017.

4. M.A. Dominguez, J.L. Pau, A. Redondo-Cubero, ‘Unusual ambipolar behavior in zinc nitride thin-film transistors on plastic substrates‘, Semicond. Sci. Technol., 34, (5), Article ID 055002, 2019.

5. S. Takayanagi, T. Yanagitani, M. Matsukawa, ‘Effect of metal mode and oxide mode on unusual c-axis parallel oriented ZnO film growth on Al/glass substrate in a reactive magnetron sputtering of Zn target’, J. Cryst. Growth 363, pp. 22–24, 2013.

6. D. Yoo, W. Jeon, J. Kim, J. Meng, Y. Yang, J. Jo, ‘ZnO thin-film transistor grown by RF sputtering using Zn metal target and oxidizer pulsing’, J. Ceram. Soc. Jpn., 125, (3), pp. 112–117, 2017.

7. W.G. Lim, C. Jo, A. Cho, J. Hwang, S. Kim, J.W. Han, J. Lee, ‘Approaching ultrastable high-rate Li–S batteries through hierarchically porous titanium nitride synthesized by multiscale phase separation’, Adv. Mater., Volume 31, 1806547, 2019.

8. Y.L. Jeyachandran, S.K. Narayandass, D. Mangalaraj, S. Areva, J.A. Mielczarski, 'Properties of titanium nitride films prepared by direct current magnetron sputtering', Mater. Sci. Eng. A, Volume 445-446, pp. 223-236, 2007.

9. X. Fan, G. Darut, M.P. Planche, X. Feng, H. Liao G. Montavon, 'Characterizations of composite titanium nitride coatings deposited by very low-pressure plasma spraying,' J. Therm. Spray Tech., Volume 28, pp. 265-272, 2019.