한국표면공학회지
*J. Kor. Inst. Surf. Eng.*
Vol. 39, No. 2, 2006.
<연구논문>

# Deposition of (Ti,Cr)N-$MoS_2$ Thin Films by D.C Magnetron Sputtering

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(Received 10 March 2006 ; accepted 1 April 2006)

## Abstract

As technology advances, there is a demand for development of hard, solid lubricant coating. (Ti,Cr)N-$MoS_2$ films were deposited on SKD 11 tool steel substrate by co-deposition of $MoS_2$ with (Ti,Cr)N using a D.C. magnetron sputtering process. The influence of the $N_2$/Ar gas ratio, the deposition temperature, the amount of $MoS_2$ in the films, and the bias voltage on the mechanical and the structural properties of the films were investigated. Wear tests were performed on the films deposited in various conditions.

*Keywords : Solid lubricant coating, (Ti,Cr)N-$MoS_2$ films, $MoS_2$, (Ti,Cr)N, D.C. magnetron sputtering*

## 1. Introduction

Wear affects the durability of cutting tools, dies and machine parts. Thus, there is a demand for better wear resistant coatings. Also, there is need for development of a coating that enables less usage of liquid lubricant since the liquid lubricant is expensive and poses an environmental concern for disposal. Solid lubricant such as $MoS_2$[1-4] has been exploited a lot to replace the liquid lubricant. We can pursue two different ways to achieve hard, solid lubricated coatings. One way is to deposit a solid lubricated film on the hard films[5]. Another way is to incorporate a solid lubricant in a hard coating[6]. Carrera *et al.*[5] reported CrN/$MoS_2$ coating. They deposited CrN film first and $MoS_2$ film was subsequently deposited. Incorporation of $MoS_2$ in a TiN matrix by D.C magnetron co-deposition has been studied by Gilmore *et al.*[6]. Kim and Cha reported incorporation of $MoS_2$ in a CrN matrix by D.C magnetron co-deposition[7].

In this study, (Ti,Cr)N-$MoS_2$ films were deposited on SKD 11 tool steel by co-deposition of solid $MoS_2$ within a (Ti,Cr)N matrix. Influence of process parameters such as the $N_2$/Ar input gas ratio, the deposition temperature, and the bias voltage on the chemical and physical properties of CrN-$MoS_2$ films were investigated.

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## 2. Experimental Procedures

(Ti,Cr)N-$MoS_2$ films were produced using an unbalanced D.C. magnetron sputtering equipment. Two circular sputter sources were fixed inside the chamber each other. Titanium target of diameter 100 mm and $MoS_2$ target of 76.2 mm were attached to each sputtering source. Sixteen Cr pellet of diameter 7 mm were embedded into the titanium target at the erosion zone to form a mosaic target. A sample holder, which could be rotated to enable voltage bias, was located at the center of the chamber. The substrate to target distance was 95 mm.

After the chamber was evacuated to $1.3 \times 10^{-4}$ Pa using a rotary pump and a diffusion pump, argon was introduced to maintain a working pressure. The SKD 11 steel (1.5% C, 11.5% Cr, 0.8%Mo, 0.9% V, Fe bal.) specimens were polished and degreased ultrasonically in alcohol. Before deposition, the specimens were plasma etched for 40 min with 600 mA (cathode surface area: 24 $cm^2$) at a pressure of 114 Pa and 400 V. Then, the (Ti,Cr)N-$MoS_2$ film was deposited on a SKD 11 steel substrate.

To determine the effect of nitrogen partial pressure, the $N_2$/Ar gas ratio of inlet gases was varied from 0.4 to 0.7. By varying the current ratio of $MoS_2$ over TiCr, the influence of $MoS_2$ content of the film on the structural and mechanical properties of (Ti,Cr)N-

$MoS_2$ film was investigated. Field emission scanning election microscope (JEOL, JSM-820) was used to observe the surface and cross-section morphology of the films. The hardness of the film was measured by a Vicker's hardness tester with 25 g load. When wear resistance was measured by a ball-on-disc type wear tester, the test condition was 100 rev/min, 3 N load, 40~50% relative humidity.

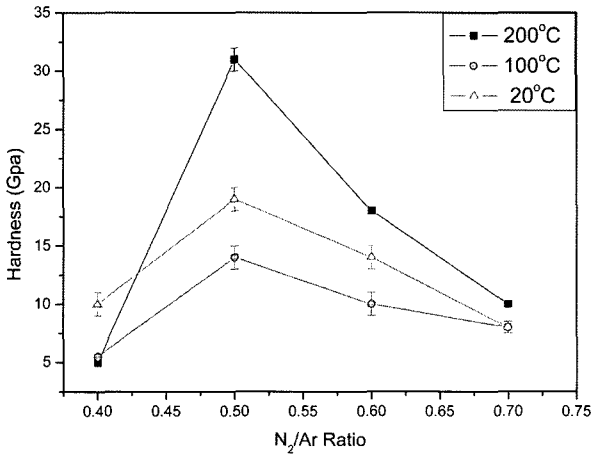



Fig. 1. Hardness of (Ti,Cr)N-$MoS_2$ films deposited at various $N_2$/Ar gas ratios of inlet gases and various temperatures.

## 3. Results and Discussion

TiCrN films were deposited by varying the ratio of Ti/Cr in the TiCr target. The ratio of 70/30 of Ti/Cr gave about equal amount of Ti and Cr (approximately 24 at. %) and high hardness. Therefore, this ratio was selected to deposit (Ti,Cr)N-$MoS_2$ thin films in the subsequent experiments. The hardness levels of the (Ti,Cr)N-$MoS_2$ films deposited at various $N_2$/Ar gas ratios of inlet gases and various temperatures are shown in Fig. 1. The highest hardness level was observed at the $N_2$/Ar gas ratio of 0.5 and deposition temperature of 200°C. The surface morphology of (Ti,Cr)N-$MoS_2$ films deposited at 200°C using various $N_2$/Ar gas ratios of inlet gases are shown in Fig. 2 and XRD diffractograms of these films are shown in Fig. 3. (Ti,Cr)N (111) peak was only observed at $N_2$/Ar gas ratio of 0.4. The films had homogeneous fine structure. At $N_2$/Ar gas ratio of 0.5, (Ti,Cr)N (200) peak was noticeable which yielded coarse chunk like structure. At $N_2$/Ar gas ratio of 0.6, (Ti,Cr)N (111), (Ti,Cr)N (200) and Ti (110) peaks were observed which could result in increased residual stress because of different orientation of these crystals. Actually the films had some partial cracks. Coarse chunks developed

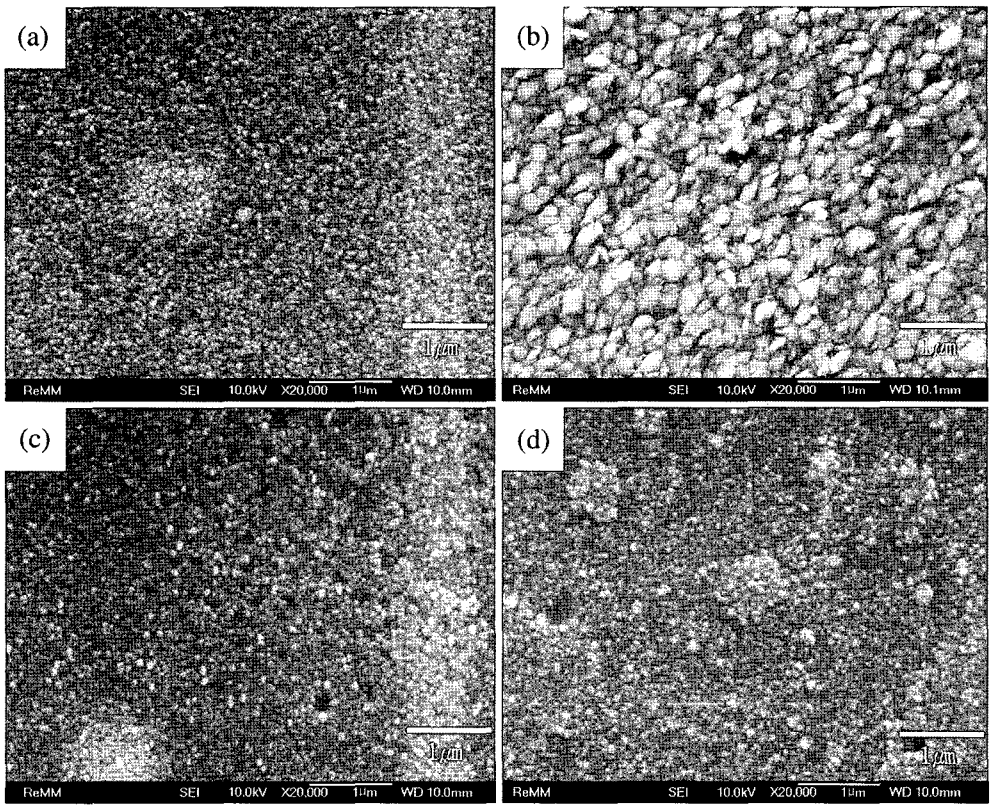



Fig. 2. Surface morphology of (Ti,Cr)N-$MoS_2$ films deposited at 200°C with various $N_2$/Ar gas ratios of inlet gases; (a) 0.4, (b), 0.5, (c) 0.6, (d) 0.7.

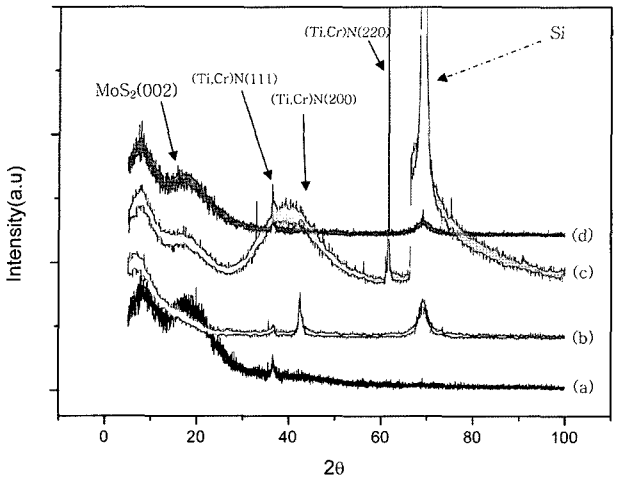
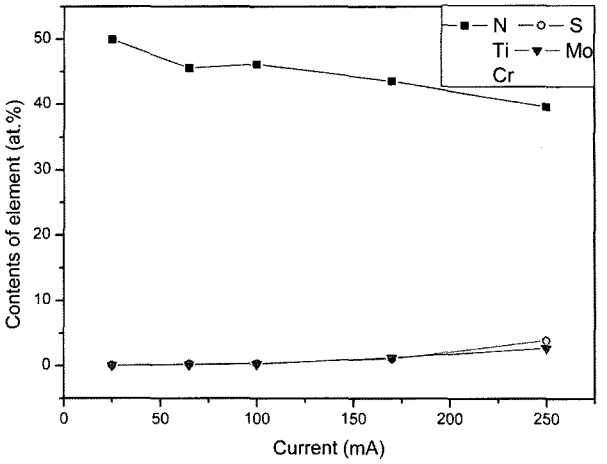



Fig. 3. XRD diffractograms of (Ti,Cr)N-$MoS_2$ films deposited at 200°C with various $N_2$/Ar gas ratios of inlet gases; (a) 0.4, (b) 0.5, (c) 0.6, (d) 0.7.




| | 25mA | 65mA | 100mA | 170mA | 250mA |
|---|---|---|---|---|---|
| Mo(at%) | 0.0048 | 0.116 | 0.217 | 1.24 | 2.72 |
| S(at%) | 0.0098 | 0.225 | 0.336 | 1.74 | 3.01 |
| Stoichmetry | $MoS_2$ | $MoS_{1.9}$ | $MoS_{1.5}$ | $MoS_{1.4}$ | $MoS_{1.1}$ |

Fig. 5. EPMA analysis of (Ti,Cr)N-$MoS_2$ films deposited with various $MoS_2$ currents.

in the film deposited with $N_2$/Ar gas ratio of 0.50. The films spalled out at other gas ratios. This could be due to the formation of brittle β-$Cr_2N$ or β-Ti.

$MoS_2$ content in the composite film was varied by applying different currents to the $MoS_2$ target. Surface morphology and EPMA analysis of (Ti,Cr)N-$MoS_2$ films deposited with various $MoS_2$ currents are shown in Fig. 4 and Fig. 5, respectively. $MoS_2$ contents in the films at low $MoS_2$ currents were quite low. However, surface morphology of these films clearly shows angular structures by addition of $MoS_2$. Hardness of the (Ti,Cr)N-$MoS_2$ films deposited with various $MoS_2$ current is shown in Fig. 6. The hardness of the film decreased with the increase of $MoS_2$ current. XRD diffarctograms of these films are shown in Fig. 7. Intensity of (Ti,Cr)N (111) peak became strong with increased $MoS_2$ content whereas (Ti,Cr)N (200) decreased a little with increased $MoS_2$ content. When

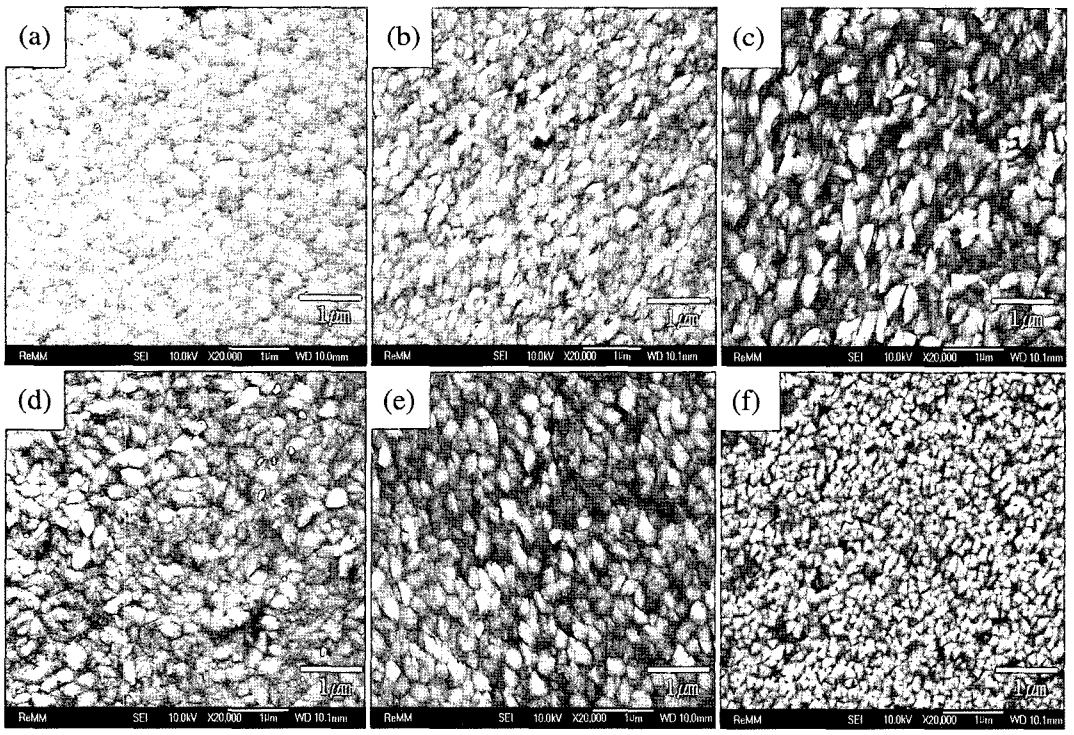



Fig. 4. Surface morphology of (Ti,Cr)N-$MoS_2$ films deposited with various $MoS_2$ currents; (a) 0 mA, (b) 25 mA, (c) 65 mA, (d) 100 mA, (e) 170 mA, (f) 250 mA.

(Ti,Cr)N (111) peak is strong, the surface morphology had fine structures which was also observed by Huang *et al.*[8]. It was reported that the grain size is small when the film had TiN (111) orientation. The grain size became coarse with the appearance of TiN (200). The film became less crystalline with the increase of $MoS_2$ current resulting in decreasing hardness. Some of the Cr atoms replaced Ti atoms within the TiN lattice in the range of over the 2 at. % Cr which forms a solid solution of (Ti,Cr)N. The TiN peaks almost overlapped with the CrN peaks[9,10].

Wear test of these films was performed as shown in Fig. 8. Films deposited with currents of 25 mA showed good wear resistance. Spalling of the film

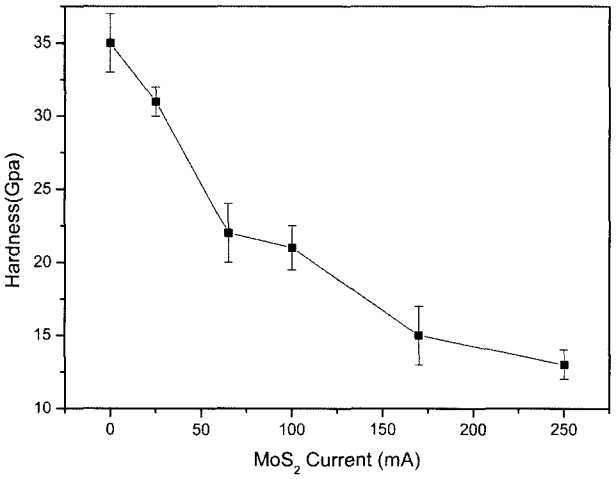



Fig. 6. Hardness of (Ti,Cr)N-$MoS_2$ films deposited with various $MoS_2$ currents.

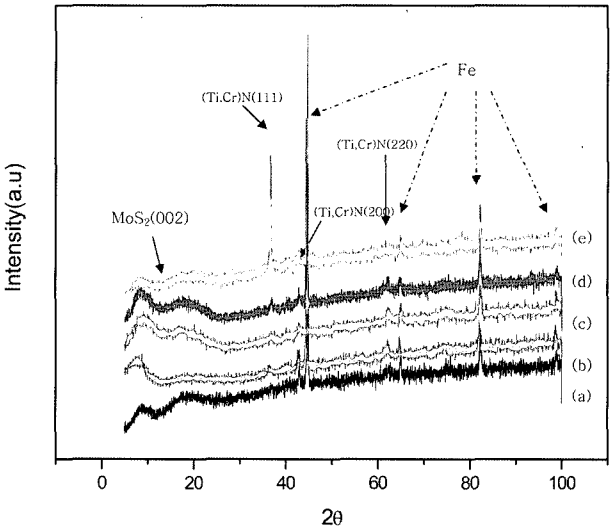



Fig. 7. XRD diffractograms of (Ti,Cr)N-$MoS_2$ films deposited with various $MoS_2$ currents; (a) 0 mA, (b) 25 mA, (c) 65 mA, (d) 100 mA, (e) 250 mA.

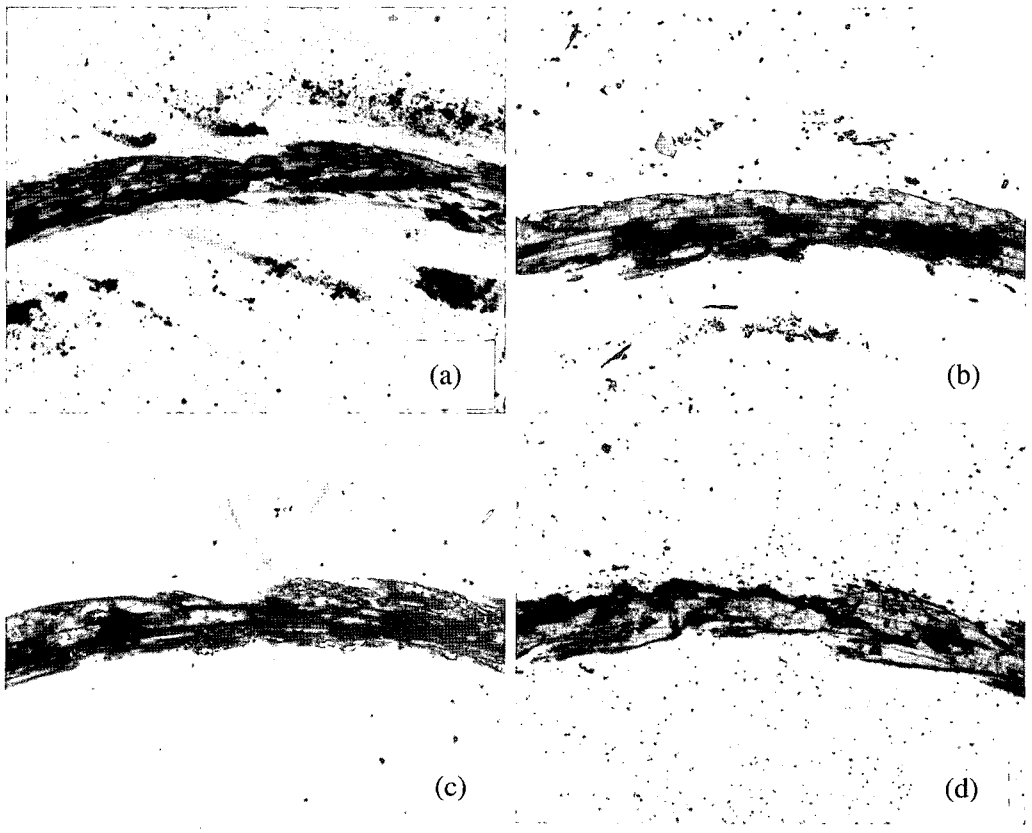



Fig. 8. Optical micrograph of wear track of (Ti,Cr)N-$MoS_2$ films deposited with various $MoS_2$ currents; (a) 25 mA, (b), 65 mA, (c) 100 mA, (d) 250 mA.

increased with the increase of $MoS_2$ current resulting in the complete spalling of the film deposited with 250 mA $MoS_2$ current. $MoS_2$ films shows superior wear resistance and adhesion in a vacuum or where there is no moisture[11]. In the present experiments, wear track spalled more with increased $MoS_2$ content. When $MoS_2$ current was increased, more $MoS_2$ lumps were seen on the surface of the film. During the wear test, these lumps cracked by partial oxidation which deteriorated the wear resistance of the films. The $MoS_x$ films prepared by sputtering does not form a stoichiometric $MoS_2$ composition. The value of x was in the range of 1.5~2.1. Oxygen easily substituted the sulfur deficient sites and forms the Mo-O-S structure, which causes degradation of tribological property[12,13]. EPMA analysis indicates that $MoS_2$ forms with 25 mA $MoS_2$ current. With the increase of $MoS_2$ current, the stoichiometry varies from $MoS_2$ to $MoS_{1.1}$. EPMA analysis indicated that the amount of molybdenum was 0.0048 at. % and sulfur, 0.0098 at. % which resulted in $MoS_2$ at 25 mA $MoS_2$ current. $MoS_{1.9}$ was formed at 65 mA and $MoS_{1.5}$ at 100 mA, and $MoS_{1.1}$ at 250 mA.

(TiCr)N-$MoS_2$ films were deposited with the change of the bias voltage up to −200 V. The hardness of these films are shown in Fig. 9. Surface morphology of the films were investigated. Coarse grains are observed at −50 V bias. With the increase of bias voltage, the hardness dropped due to the collapse of the structure. XRD diffractogram of the films are shown in Fig. 10. A strong (Ti,Cr)N (111) peak and a weak (Ti,Cr)N (200) peak were observed at 0 V. (Ti,Cr)N (200) peak became strong and (Ti,Cr)N (111) peak diminished at −50 V. (Ti,Cr)N (111) peak became strong with the increase of the bias voltage.

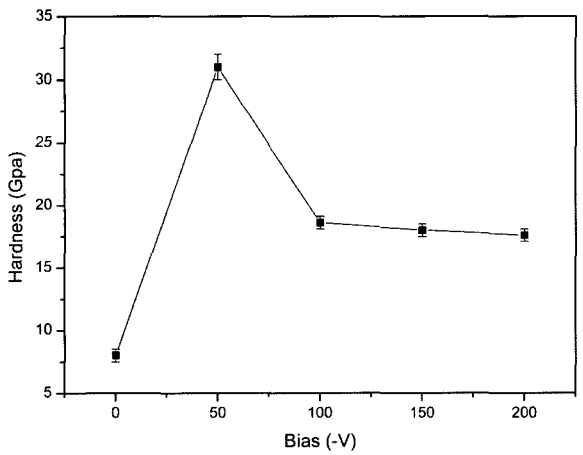



Fig. 9. Hardness of (Ti,Cr)N-$MoS_2$ films deposited at various bias voltage.

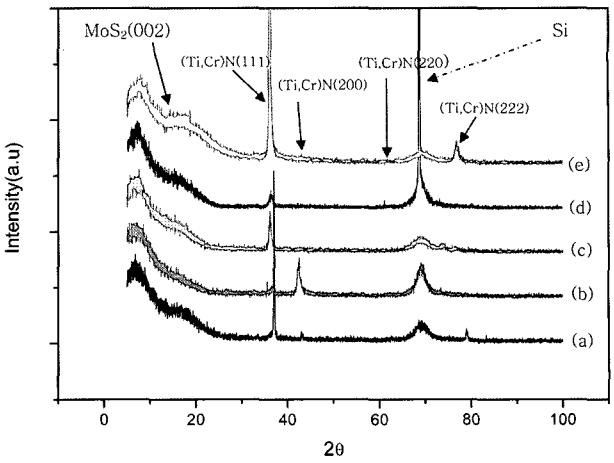



Fig. 10. XRD diffractograms of (Ti,Cr)N-$MoS_2$ films deposited at 200°C with various bias voltage; (a) 0 V, (b), 50 V, (c) 100 V, (d) 150 V, (e) 200 V.

The direction <111> is the hardest orientation in TiN. However, the experimental result shows that it is not valid with (Ti,Cr)N-$MoS_2$ films which has a soft compound like $MoS_2$.

## 4. Conclusion

(Ti,Cr)N-$MoS_2$ films were deposited on SKD tool steel using an unbalanced D.C. magnetron sputtering equipment. The highest hardness level was observed at the $N_2$/Ar gas ratio of 0.5 and deposition temperature of 200°C. At $N_2$/Ar gas ratio of 0.5, (Ti,Cr)N (200) peak was noticeable which yielded coarse chunk microstructure. The films became less crystaline with the increase of $MoS_2$ content which resulted in the decrease of the hardness of the films. Wear resistance deteriorated with the increase of $MoS_2$ content. The films deposited with −50 V bias yielded the highest hardness. The hardness of the films decreased with the increase of bias voltage due to the collapse of the structure.

## Acknowledgement

This work was supported by Grant No. R-11-2000-086-0000-0 from the Center of Excellency Program of the Korea Science and Engineering Foundation & Ministry of Science and Technology.

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