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Wettability and Optical Property Analysis of Hafnium Nitride Coating

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ABSTRACT

Today's trends of coating technology will improve day by day. In the field of surface engineering enhancing supreme excellence of surface will achieve by using differential coating technology. In the coating phenomenon sputtering technique is one of the useful fundamental method for coating process. Sputtering is a physical vapor deposition technique. In which substrate material coated with the physical process. Physical vapor and chemical vapor are the deposition techniques which is used for the coating from many years ago. Hafnium nitride coating should be carried out with the use of sputtering technique. After coating with the hafnium nitride using different instruments the results should be declared. For the property analysis narrator use the SEM, XRD etc.

KEYWORDS: coatings, hafnium nitride, wettability, optical property

INTRODUCTION

Coating is process of wrapping of substrate surface using different coating process for decorative purpose or functional purpose. It defends the substrate surface from physical environment, dust, and other external impurities. It causes change in properties of substrate surface.Hf is the symbol for the hafnium as a chemical element and the 72 is registered as the atomic number for it. [1]. Hafnium is the element which is processed from the minerals of the zirconium. Filament and the electrodes are one of the application which uses the hafnium. In the manufacturing process, oxides of the hafnium are used in semiconductor. That are useful for the integrated circuit at 45nm and smaller length. It is also used in coating of ceramics and cutting tools. For special applications contain hafnium in combination with niobium, titanium, or tungsten super alloys are used [2].

In the HfNcoating the larger amount of hafnium and remaining is nitride mix with each other. It has a capacity to withstanding under higher loading situations. It provides the good adhesion to the substrate after the coating. Hafnium has a melting point 2231 ^{0}C hafnium nitride has formulae weight is 192.497 and consider into the nitride class[3].It has a yellow brown color.it has appearance like crystalline solid. From the element analysis it is found that hafnium percentage is 92.72 and nitride is 7.28.

Hafnium nitride coating:

Hafnium nitride is hard protective coating. Which protect the shielded surface. Hafnium nitride has a good adhesion property after assured point. At the elevated temperature it provides the hardness. As the indentation depth increase the number of layer will also increase. After the critical load fracture will generate on the treated surface [4].At low substrate temperatures (150-250 °C) with homolептictetrakis (dialkylamido) metal

(IV) complexes and ammonia are processed for the producing smooth and conformal coating of high nitrides from hafnium and zirconium. Silicon, glass, are the useful substrate for the effective coating [5].

Jill s. backer et.al. (2004) are inspected some properties of hafnium nitride by vitiating pumping speed and the pressure of reactor. They observed that increase in thickness of film will lead to increase in number of cycle and also deposition temperature. On the other hand, the higher nitrides of hafnium andzirconium, M3N4, are registered as the semiconductors. Films of hafnium and zirconium placed on the metal alklide and ammonia by the atomic layer deposition technique in the mild condition of the 1500 to 2500c in non-corrosive and nonoxidizing atmosphere [5].

In the study of William's experiment he used reactive magnetron sputtering with the very high rate to produced thin films. Atmosphere for the process were created with the very large amount of nitrogen concentration. As the variation in the nitrogen contain generated were affect the intensity of darkness of the colour.in the starting it shows the pale yellow and with the higher amount of nitrogen were changed theintensity of color. The rich golden color have large cell size as compared with the bulk material.[6].

WILLIAM D.SPROUL Et. Al. (1984) classifies some of the changes into the hafnium nitride coatings. They change the comparatively n level from 1 to 10 and (111) d specing from 2.627 to 2.661 with the temperature variation of 1000^0C. After the experiment high hardness were investigated. Annealing were carried out on the sample which drop the cell size same as the bulk material.For the reaction barrier composites of the hafnium nitride were measured as the suitable material. Hafnium nitride film generated on the niobium and high density graphite substrate with the use of deposition method like reactive magnetron sputtering. [3].

In this paper of A. Ravi Shankar Et.al. (2012), the stretched out parameters were utilized to cover high thickness graphite and on niobium substrates with hafnium nitride. The result after the philosophy communicates that the hafnium nitride films were secured on HD graphite and niobium substrate with the 2.8mm thickness. X-ray beam diffraction (GIXRD) and X-ray beam photoelectron spectroscopy (XPS) were used after the method to check the openness and consistency of the hafnium nitride. Si (100) covering with the hafnium nitride were investigated with the usage of XRD system. The atomic power amplifying focal point and checking electron amplifying instrument are used to mull over the surface morphology of the HfN covering on the substrate surface. Graphite substrate has cut down connection quality when appeared differently in relation to high thickness niobium substrate. This result was articulated in the wake of doing scaled down scale scratch test [7].

Reformation of variables were considered on Si (100) to pick up nano crystalline HfN of thickness 3 mm. XRD Pattern of the covers proved the presence of HfN on HD graphite and niobium substrates with a Face Cubic Center structure. Grain size of the covers was detected to be 55.1 °A and 46.4 °A on overwhelming thick graphite and niobium substrate comparably. In this trial the sincere weight regards found for HfN covering on HD graphite and niobium substrates are (+/ -)0.4146 GPa and (+/ -)0.0763 GPa, independently, which suggests especially compressive stress with HD graphite substrate and versatile stress with Nb substrate [8].

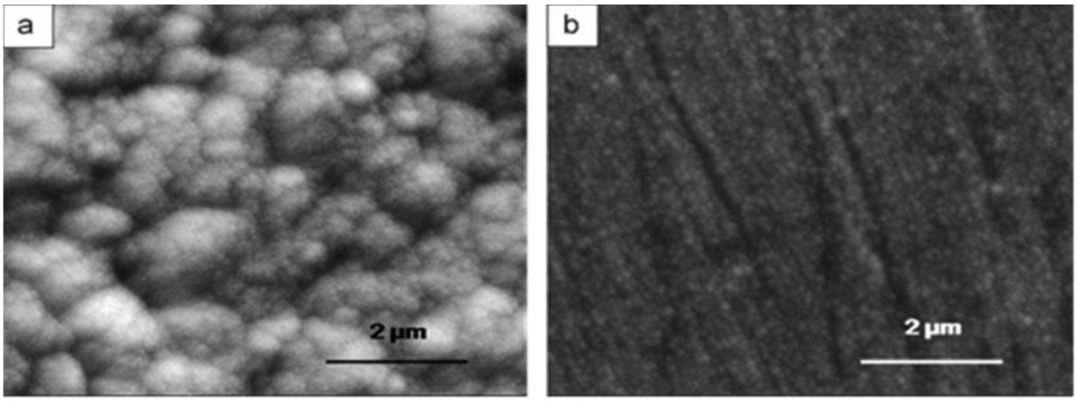

Figure 1 *Image shows the result of micro scratch test*

Samad M. Edlou Et.al.(2013) published paper displays some useful result for the optical property and mechanical property of hafnium nitride coating. In this DC reactive magnetron sputtering with the Base pressure 3*10-8 torr and at the room temperature film adhesion to merged silica. TiN films has a optical property same as the Ag and the ZrN and HfN have the optical property which matches with the Au. Comparing the two groups transition metal have the superior mechanical property as well as chemical property. They were poor in optical and electrical properties [9].

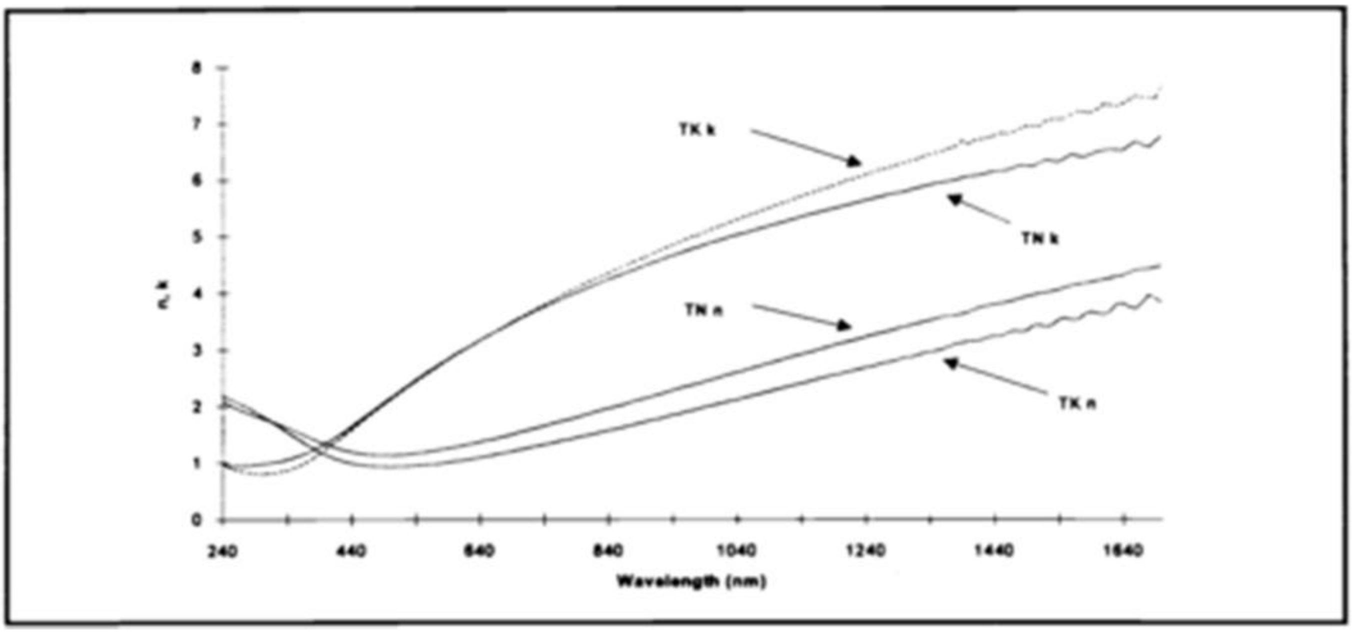

Figure 2 *optical constant TK and TN, VASE measured HfN*

Maria Stromme Et.al. (1994) completed covering of hafnium nitride using reactive magnetron sputtering with deposition rate of 2.1 nm/s. With altered wavelength (nm) value of optical constant (n & k) increase. TiN, ZrN and HfN, it is anticipated that lone the electrons over the base in the thickness of states add to the plasma recurrence [10].

The spectral energy range 0.1 to 6.2 eV have been estimated for the reflectivities of titanium nitride, hafnium nitride. The optical constants have been fearless by methods for a Kramers-Kronig examination. A separating into interband changes and permitted electron execution was done. Optical properties of carbide and nitrides in the fourth and fifth section in to the intermittent table are fascinating. There is vast number of examination for optical property of TiN covering yet contrasted with this not very many are for the HfN and ZrN. It is likewise of an extraordinary enthusiasm to examine the optical nature of CVD covered films[11].

In the ANDREAS ZERR et.al. (2003) give the outcome that high-weight blend is a serious procedure for the introduce of interesting materials with high adaptable moduli and hardness. What's more, such materials may demonstrate empowering warm, optoelectronic, semiconductuing, alluring or superconducting properties. Usage of high weights prompts the advancement of thick stages with higher coordination amounts of atoms, with high adaptable moduli and, perhaps, with high hardness. The being of c-Zr3N4and c-Hf3N opens up another likelihood in high-weight blend since they could be the essential people from a greater social occasion of advance metal and lanthanide nitrides showing captivating utilitarian appealing or superconducting properties [4].

K.Volz et.al. (1999) stated that using 10 KW input power and pressure of 2.0*10-3 with ion deposition method tested the properties of hafnium nitride coating. Hafnium evaporation under concurrent nitrogen ion bombardment result in the development of HfN with cubic structure (B1). [12]

Table 1 Investigation of the research group that effect of using different parameters and different deposition method on optical and wettability property of hafnium nitride based coating

Research groups (Years)	Deposition Technique	Parameters	Properties examined
G. Lo pez Et. Al.(2004)[13]	Magnetron sputtering	Temperature: 400 to 700^{0}C Load: 50,100,200	It was uncovered that ZrN layers set by methods for bolted field precarious magnetron-sputtering particle plating procedure could recoup the wear and grinding execution of the AISI 1045 substrate at room temperature.
ZhiqingGu Et.al.(2015)[14]	RF reactive sputtering	Pressure: 4*10^{-4} RF power : 150 W work pressure : 1.0 Pa substrate negative bias : -80V substrate temperature : 200^{0}C	We have effectively perceived the "nitrogen-rich" period of hafnium nitride (HfN) films through a blend of SAED, HRTEM, Raman, XRD and XPS estimations and the primary standard figurings and uncovered, out of the blue, the points of interest and instruments of the stage progress from the rocksalt d-HfN to the "nitrogen-rich" structure.
B. Karlsson Et.al.(1982)[15]	CVD	Total system pressure: ^0.1 MPa. Temperature: 1100,1150,1170 Time(H): 8,10,14	The optical constants have been fearless by methods for a Kramers-Kronig investigation. A separating into interband changes and free electron conduct was completed
S. M. Aouadi Et.al.(2004)[16]	Reactive unbalanced Magnetron sputtering	System pressure: 1*10^{-5}Pa dc power supply: 500 WAr partial pressure: 260 mpa	The microstructural, compound, and optical properties of these coatings were examined by methods for XRD, XPS, and SE. The natural and stage arrangements, optical constants, and transport properties were inferred as a component of the nitrogen Content
Yao Chen Et.al.(2008)[17]	Plasma sprayed technique	Load: 25 µNs^{-1} up to 150 µN Temperature: 1500^{0}C Nitrogen pressure: 170 mpa	For HIPedHfN coating, the elastic modulus (E) and yield strength risewhile the hardness (H), H/E relation and fraction of the elastic work reduction. pile-up around the indent as compared to AssprayedHfN
M. Vargas Et.al.(2014)[18]	Sputter deposition	base pressure: of 10^{-6} Torr. Power: 100 W Deposition time: 45 min	The consistent film unevenness follows a falling trend with increasing in Ts. The packing density and structural HfO_2films increasing with Ts.
Chaoquan Hu et.al.(2016)[19]	Redio frequency sputtering	Deposition time: 160min	Whole deposition process of 160 min, the mixed-phase films reserve a steady development where the vertical and horizontal developmentamounts are nearly the same.

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c.escobar et.al.(2014) [20]	Magnetron sputtering	Cutting speed: 110m/min Feed rate : 0.07mm/rev Depth of cut: 0.5mm Coolant: dry	As the bilayer number will increase hardness also increase with it. Elastic modulus will increase with increase In bilayer number. Friction coefficient will decrease in increase in bilayer number.
ZhiqingGu Et.al.(2015)[14]	Reactive sputtering	Theoriticle 2ϴ: 32.80,38.01, 42.76, 55.03, 62.06 ,78.29 ,90.56 Theoretical d: 2.73, 2.37, 2.11, 1.67, 1.49, 1.22, 1.08	We have emphatically perceived the "nitrogen-rich" phase of hafnium nitride (HfN) layers through a mix of SAED, HRTE, XRD and XPS estimations and the primary standard controls and revealed, out of the blue, the points of interest and gadgets of the stage progress from the rocksalt d-HfN to the "nitrogen-rich"structure.
SUSHANT K RAWAL Et.al.(2013)[21]	Rf magnetron sputtering	For water ãL(mN/m): 72.8 ãL^d(mN/m) : 21.8 (ã^P L): 51 For Diiodomethane ãL(mN/m): 50.8 ãL^d(mN/m): 50.8 (ã^P L): 0	The set titanium and zirconium oxynitride films are delicate to the power change of the two targets. It in the end prompts increment in the declaration rate and surface brutality of the layers. The most decreased contact point estimation of 67.4◦ depicting hydrophilic nature and more important contact edge of 97.5◦ for hydrophobic layers was perceived.
Simons Et.al.(2013)[9]	DC magnetron sputtering	Base pressure: 3*10^{8}torr Deposition pressure: 2.8 to 5*10^{-4} Incidence angle: 70,75,80	Reactive DC magnetron sputtering was utilized to make thin movies of TiN, ZrN and HfN at room temperature. The movies show optical properties alike to respectable metals. The structure of TiN, ZrN and HfN and their acclimating optical and electrical properties can be changed by controlling nitrogen incomplete weight amid statement.
B. Karlsson et.al.(1982)[15]	Chemical vapour deposition	For HfN PH2: 0.386 PN2: 0.610 PMC14 0.004 Temperature: 1150	The reflectivity of TiN, ZrN and HfN have been stately in the unearthly vitality 0.1 to 6.2 eV. The optical constants have been courageous by techniques for a Kramers-Kronig examination. A valedictory into interband advances and free electron direct was finished.
S. M. Aouadi et.al.(2004)[16]	Reactive magnetron sputtering	System pressure of = 1*10^{-5}Pa power supply = 500 W dc Ar partial pressure = 260m pa	The compound, and optical properties of these coatings were analyzed utilizing XRD, XPS, and SE. The optical coefficients decided in this examination will be utilized as a part of accumulation with genuine time spectroscopic ellipsometry to show and control the advancement of tantalum nitride films.

A. GRILL Et.al.(1983)[22]	RF sputtering	Pressures: 8 and 20 mTorr deposition rate: 190 A^0min^{-1}	Connection of made silicon nitride and hafnium nitride to cemented 440C steel, as fair by the scratch test, is delivered by a decreased sputtering weight and by pre-oxidizing the substrates. The hafnium nitride indicates bendable disillusionment and remains in the path at loads greater than two overlap the essential load.
William D. Sproul Et.al.(1986) [23]	Reactive sputtering	TiN Deposition rate: 4400(ang/min) Target power(KW): 10 ZrN Deposition rate: 4000(ang/min) Target power(KW): 8 HfN Deposition rate: 5800(ang/min) Target power(kw) : 10	All of these coatings have hardness values that are much higher than those listed for the bulk materials, and all of the coatings have thesodium chloride structure with a (Ill) preferred orientation. Hot hardness tests show that HfN is harder than ZrN up through 800 'C, but at 1000^0C ZrN is harder than both HfN and CVD AI2 O3.
Chaoquan Hu Et.al.(2016) [19]	RF sputtering	Deposition time 160min Film thickness: 28 to 423nm	Amid the testimony technique of 160 min, the blended stage layers save an unfaltering development where the vertical and flat development rates are nearly the same; in the interim, the two single-stage films bear a change from consistent to precarious improvement offering ascend to smooth to high unpleasantness advancement in surface morphology.
YasuhitoGOTOH Et.al.(2003)[24]	Sputtering	Background pressure: 4.0 $*10^{-4}$Pa Argon gas pressure during deposition: 0.5–5 Pa Substrate temperature: RT(not controlled): -500^0 C Input rf power: 30–100 W	We originate that film composition showed little deviation from the stoichiometry. Despite the above result, it was possible to control the film properties such as crystal orientation, stress, and electrical resistivity.
FLMartinez Et.al.(2007) [25]	High pressure reactive sputtering	Substrate temperature: 200^0C RF power: 60W Deposition time: 30 min	We have characterized the optical and basic properties of HfO2 thin movies and thought how these properties are misrepresented by the decision of

			sparkle discharge gas utilized for affidavit. We achieve that the presentation of oxygen into the argon sparkle discharge indorses zone 1 polycrystalline development, while the structure of the movies set with a perfect argon plasma is undefined.
Aditya Aryasomayajula Et.al.(2006) [26]	Pulsed DC magnetron sputtering	Power: 1KW Frequency: 20 KHz Time: 120 min Pressure: 3pa	It can be understood that thedeposition amountrisesmonotonically with anrise in sputtering power.
G. Auner Et.al.(1984) [27]	RF Sputtering	Deposition temperature: 200^0C Substrate temperature: 300^0C Pressure: 5mTorr	Relative microhardness willincrease at definite point anddecrease with increase in ionbombardment. The films whenimplanted with Kr designatedmaximum improvement inmicrohardness for N2pressures corresponding toStoichiometricHfN.
Leandro Garcia Gonzalez et.al.(2014) [28]	Sputtering	Temperature: 25,100,200,300,400 500 Hardness: 15.8Gpa Electric resistivity: $1.23*10^{13}$	Hardness drop with lessening in relative space profundity. Temperature increment will cause to decrease in hardness. The consumption protection is high for thin layers HfN. In spite of the fact that the contact coefficient inclinations to rise, stay in an agreeable range And progressed than a few paired and ternary hard covers.
Jiann-ShingJeng et.al.(2009)[29]	sputtering	Base pressure: $3*10^{-6}$torr Working pressure: $7*10^{-3}$torr Input power: 100W Substrate bias: 100 & 200V	For Hf-N films set at different N stream extents, the resistivity diminishments with creating substrate slant, as a result of the low affirmation rate of Hf-N layers, the oxidation of layers fundamentally rises. The material property of responsively sputtered hafnium-nitride proficiently turn on the sputter parameters.
T. Kanzawa et.al.(2009) [30]	RF magnetron sputtering	Background pressure: $4*10^{-4}$ Argon gas pressure: 1.0, 2.0 Pa Redio frequency power: 30, 50, 70 W Substrate temperature: room temperature to 600	Electrical resistivity showed strong association with substrate temperature. If the substrate temperature increasing than the electrical resistivity decreases.
M. Kodama Et.al. (1978) [31]	Reactive sputtering	Reactive gas: N2 Pressure: $5.8*10^{-4}$ Substrate temperature: 550 ^{0}C	HfN-coated tools has very low wear rate compare to the TiC-coated tools. And the ion-plated TiN/TiC-coated tools. Also in the appearance HfN looks better than the TiC coated tool

Conclusion :

Hafnium nitride coating delivers, decrease in hardness with decrease in relative indentation depth. Temperature increament will cause decreament in hardness. The corrosion resistance is high for thin films HfN. The friction constant tends to increase in a satisfactory range. After seprating transition metal and free electron behavior of atoms are investigated. We conclude that strength hardness and other mechanical properties as well as chemical properties are good but the optical and electrical property are not good as mechanical property of the transition metal. For the wettability it has been new perception in hafnium nitride coating. It should be measure by variating contact angle and get the results for certain wettability value.

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