

Surface Free Energy Effects in Sputter-Deposited WN_x Films

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WN_x thin films have attracted much attention for semiconductor IC packaging molding dies and forming tools due to their excellent hardness, thermal stability. WN_x thin films with $WN_{0.46}$, $WN_{1.03}$, $WN_{1.52}$, $WN_{1.91}$, $WN_{2.54}$ were prepared using radio frequency (RF) sputtering. The experimental results showed that the contact angle at 20°C go up with raising N_2 content to 116.7° at beginning, corresponding to $WN_{1.91}$, and then drop off. In addition, the contact angle components decreased with increasing surface temperature. Because increasing surface temperature disrupts the hydrogen bonds between water, Diiodomethane, Ethylene glycol and the films and these liquids vaporize gradually. The total SFE at 20°C decrease with N_2 content to raise to 37.6 mN/m($WN_{1.91}$) at the start, and then increase. Because a larger contact angle means that a weaker hydrogen bonding, resulting in a lower SFE. The polar SFE component has same trend with total SFE, but the dispersive SFE component is on the contrary exactly. The polar SFE component is also lower than the dispersive SFE component. This is resulting from hydrogen bonding being polar. The total SFE, dispersive SFE and polar SFE of WN_x films decreased with increasing surface temperature. This is because liquids evaporation on the surface, disrupted hydrogen bonds and surface entropy increasing with increasing temperature. The film roughness has an obvious effect on the SFE and there is tendency for the SFE to increase with increasing film surface roughness. Because SFE and surface roughness can be expressed as a function in direct ratio. [doi:10.2320/matertrans.MRA2007095]

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1. Introduction

Today transition metal nitride ceramic thin films are commonly used as protective coatings to improve the lifetime of tools and components.¹⁻⁶ Tungsten nitride (WN_x) coatings gained interest due to their high hardness, advanced tribological properties, thermal stability and good performance in corrosive environments, and may have a good anti-adhesive effect (high contact angle, low surface free energy), that can be applied to injection molding components.⁷ For the semiconductor IC packaging molding application, the surface free energy of these coatings is very important. Because the mold releasing capability is directly associated with the surface free energy between the coating surface and product material. In the IC molding packaging process, the packaging material (Epoxy Molding Compound, EMC) captures the microcircuit matures and adheres to the surface of the packaging forming tools. Because of the surface sticking effect one hour is required for cleaning the surface of the packaging forming tools after the packaging system has operated for twenty four hours. Heavy sticking effects can cause failure in IC molding packaging. Therefore, longer service life is expected and higher productivity has become an economic necessity. Developing low surface free energy coating materials that have potential for improved performance has become extremely important. Because of environmental awareness and the ever increasing design complexity of integrated circuits, adaptable coating materials and technologies are required for packaging dies.

In the WN_x system, few data has been published on the surface free energy at different temperatures. This paper discusses the effect of composition and surface temperature on the contact angle and surface free energy of WN_x coatings at temperatures in the range 20–170°C. The investigated films are compared with different WN_x surface roughness. This work has potential relevance in terms of design and injection molding industrial equipment operation.

2. Experimental Details

The WN_x films (2 μ m thick) were deposited on Si(100) substrates using a radio frequency (RF) sputter system with Tungsten target and the amount of N_2 at 5, 10, 15, 20, 25 sccm, Ar at 25 sccm. The substrates were Ar plasma ion cleaned prior to deposition. The base pressure of the sputtering system was 4×10^{-3} Pa. During sputtering, the total chamber pressure were 5×10^{-1} Pa. The films thickness was measured using an α -step 500 surface profilometer. Chemical composition was analyzed using energy dispersive spectroscopy (EDS).

The contact angles were obtained using the sessile drop method with a Dataphysics OCA-20 contact Angle analyzer. This instrument consists of a CCD video camera with a resolution of 768×576 pixel and up to 50 images per second and a temperature controlled environmental chamber. The digital drop image was processed using an image analysis system, that calculated both the left and right contact angles from the shape of the drop with an accuracy of $\pm 0.1^\circ$. Three test liquids were used as a probe for the surface free energy calculations: distilled water, diiodomethane and ethylene glycol. Because distilled water, Diiodomethane, Ethylene glycol have different level polarity. This paper want to find the contact angle and surface free energy variation of these three different polar level liquids to the film. The surface tension of distilled water at 20–95°C was estimated using the following equation:^{8,9)}

$$\gamma_L = 235.8 \left(\frac{374 - T}{647.15} \right)^{1.256} \left[1 - 0.625 \left(\frac{374 - T}{647.15} \right) \right], \quad (1)$$

where $T(^{\circ}\text{C})$ is distilled water temperature. The surface tension of diiodomethane at 20–170°C were estimated using the following equation:⁸⁾

$$\gamma_L = 53.48 - 0.14154T + 4.9567 \times 10^{-5}T^2, \quad (2)$$

where $T(^{\circ}\text{C})$ is diiodomethane temperature. The surface tension of ethylene glycol at 20–170°C were estimated using the following equation:^{8,10)}

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Table 1 Test liquids and their surface tension components.

Liquids	Boiling point (°C)	Temperature (°C)	Surface tension data (mN/m)		
			γ_L	γ_L^d	γ_L^p
Distilled water, H_2O	100	20	72.8	21.8	51.0
		45	68.8	20.6	48.2
		70	64.5	19.3	45.2
		95	59.9	17.9	42.0
Diiodomethane, CH_2I_2	180	20	50.8	50.8	0
		45	47.2	47.2	0
		70	43.8	43.8	0
		95	40.5	40.5	0
		120	37.2	37.2	0
		145	34.0	34.0	0
Ethylene glycol, $C_2H_6O_2$	198	20	48.0	29.0	19.0
		45	46.0	27.8	18.2
		70	44.3	26.8	17.5
		95	42.6	25.7	16.9
		120	41.0	24.8	16.2
		145	39.3	23.7	15.6
		170	37.6	22.7	14.9

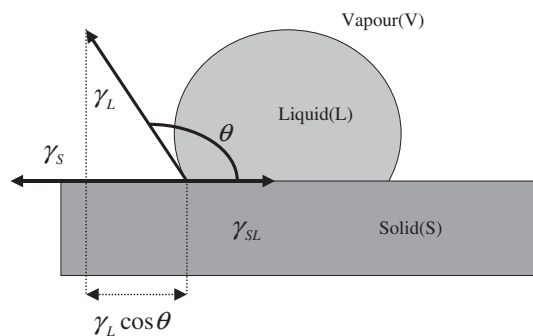


Fig. 1 Illustration of geometric parameters for determining interfacial energy.

$$\gamma_L = 48.97 - \frac{T}{15} \quad (3)$$

where $T(^{\circ}\text{C})$ is ethylene glycol temperature. In three test liquid cases, the surface tension components of test liquids at different temperatures was estimated by assuming that test liquid surface tension and its surface tension components decrease with increasing temperature at the same rate. The data for the test liquid surface tension and surface tension components at temperatures in the 20–170°C range are given in Table 1.

The surface free energy of solids may be determined by measuring the contact angles with the aid of a test fluid whose surface energy is known. This measurement technique is based on Young equation, which express the condition for equilibrium at a solid-liquid interface in 1805⁽¹¹⁾ (Fig. 1).^(12,13)

$$\gamma_L \cos \theta = \gamma_S - \gamma_{SL} \quad (4)$$

where γ_L is the experimentally determined surface tension of the liquid, θ is the contact angle, γ_S is the surface free energy of the solid and γ_{SL} is the solid-liquid interfacial energy. To obtain the solid surface free energy γ_S , an estimate of γ_{SL}

must be obtained. According to Fowkes in 1962, the total surface free energy of each phase can be split into 2 parts: a dispersive part and non dispersive part. The first part results from the molecular interaction due to London forces and the second part is due to all of the non-London forces:

$$\gamma_i = \gamma_i^d + \gamma_i^p \quad (5)$$

Owens and Wendt⁽¹⁴⁾ extended the Fowkes equation and included the hydrogen bonding term. They used geometric mean to combine the dispersion force and hydrogen bonding components:

$$\gamma_{SL} = \gamma_S + \gamma_L - 2\sqrt{\gamma_S^d \gamma_L^d} - 2\sqrt{\gamma_S^p \gamma_L^p} \quad (6)$$

From the Young eq. (4), it follows that

$$\gamma_L(1 + \cos \theta) = 2\sqrt{\gamma_S^d \gamma_L^d} + 2\sqrt{\gamma_S^p \gamma_L^p} \quad (7)$$

To obtain γ_S^d and γ_S^p of a thin film, the contact angle of at least two liquids with know surface tension components ($\gamma_L, \gamma_L^d, \gamma_L^p$) on the solid must be determined. In our case, three liquids (distilled water, diiodomethane, ethylene glycol) were used to determine γ_S^d and γ_S^p of the WN_x films as a function of the amount of N_2 increasing from 5 to 25 sccm in an industrial RF sputter system. These results and the different values for the contact angle measured using the three liquids are shown in Table 2. The surface free energy of the WN_x films is composed of a high dispersive component and a low polar component.

The roughness of the films were characterized by atomic force microscopy (AFM) in the tapping mode. The value of root-mean-square (RMS) surface roughness was evaluated over the area of $2 \times 2 \mu\text{m}$.

3. Results and Discussion

3.1 Film composition analysis

Depending on the EDS, the film of N_2 containing 5 sccm,

Table 2 Contact angles of test liquids on the films.

composition	Temperature (°C)	Contact angle (°)		
		θ_{Water}	$\theta_{\text{Diiodomethane}}$	$\theta_{\text{Ethylene glycol}}$
WN _{0.46}	20	72.1	30.1	88.6
	45	58.7	26.3	84.9
	70	66.2	25.1	80.5
	95	46.2	21.4	67.3
	120	—	24.8	72.1
	145	—	22.9	70.9
	170	—	24.1	62.5
WN _{1.03}	20	88.8	27.5	89.1
	45	77.1	25.5	82.6
	70	59.1	28.8	80.2
	95	65.2	25.2	68.5
	120	—	27.6	73.7
	145	—	22.8	62.6
	170	—	20.9	62.5
WN _{1.52}	20	105.1	26.8	85.6
	45	87.4	29.5	85.4
	70	91.3	31.5	87.8
	95	72.6	21.1	66.8
	120	—	30.7	80.6
	145	—	26.4	62.6
	170	—	20.2	58.9
WN _{1.91}	20	116.7	33.1	93.3
	45	105.6	32.1	90.3
	70	88.9	24.7	78.2
	95	93.2	15.3	56.8
	120	—	23.1	71.5
	145	—	29.6	78.3
	170	—	27.7	69.9
WN _{2.54}	20	102.1	21.2	80.8
	45	95.3	20.5	75.5
	70	78.2	19.3	70.1
	95	84.6	28.1	72.5
	120	—	18.1	64.6
	145	—	16.9	61.3
	170	—	14.2	51.2

its chemical composition follows: W : N = 68.49% : 31.51% = 1 : 0.46 (WN_{0.46}); the film of N₂ containing 10 sccm, its chemical composition follows: W : N = 49.26% : 50.74% = 1 : 1.03 (WN_{1.03}); the film of N₂ containing 15 sccm, its chemical composition follows: W : N = 39.68% : 60.32% = 1 : 1.52 (WN_{1.52}); the film of N₂ containing 20 sccm, its chemical composition follows: W : N = 34.36% : 65.64% = 1 : 1.91 (WN_{1.91}); the film of N₂ containing 25 sccm, its chemical composition follows: W : N = 28.25% : 71.75% = 1 : 2.54 (WN_{2.54}).

3.2 Contact angle values

Contact angle of the test liquids, distilled water (θ_W), diiodomethane (θ_D), and ethylene glycol (θ_E) on the WN_x films at surface temperature in the range 20–170°C are given in Table 2. Significant variations in the contact angle values were observed on WN_x films. With raising N₂ content, the

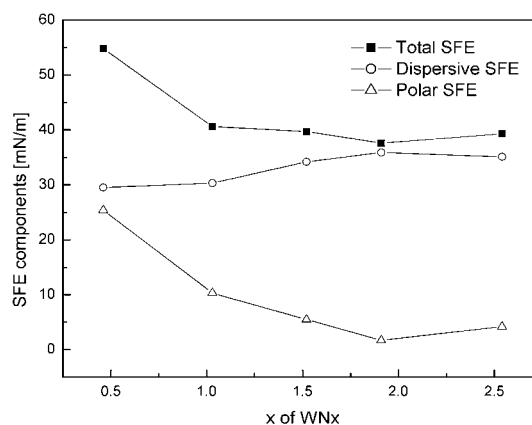


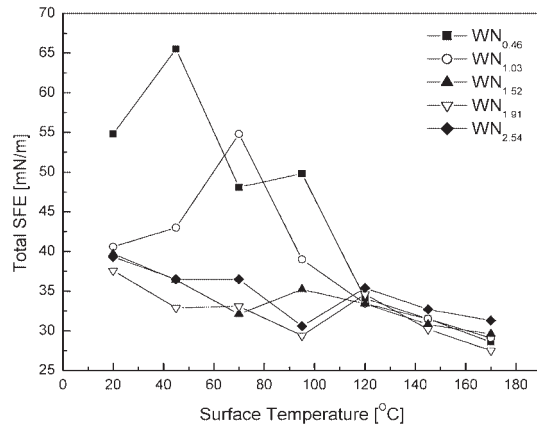
Fig. 2 Effect of composition on surface free energy (SFE) components of WN_x thin films at 20°C.

contact angle at 20°C go up to 116.7° at beginning, corresponding to WN_{1.91}, and then drop off. In addition, the contact angle components decreased with increasing surface temperature. Because increasing surface temperature disrupts the hydrogen bonds between water, Diiodomethane, Ethylene glycol and the films and these liquids vaporize gradually. According to the contact angle values the surface free energy of the samples and their dispersive and polar components were calculated using the Owens-Wendt geometric mean approach.

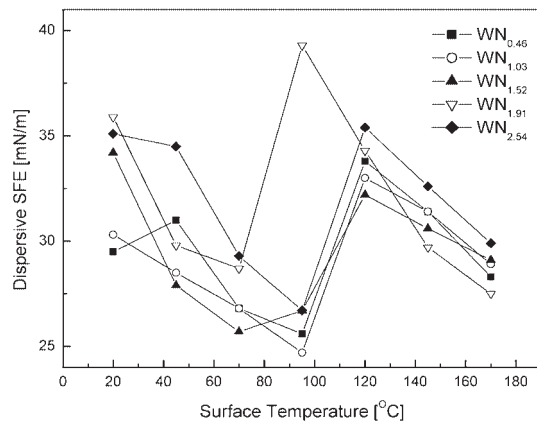
3.3 Effect of composition on surface free energy of WN_x films

Surface free energy arises from the unbalance of the force between atoms or molecules inside and interfaces. Several types of van der Waals interactions contribute to SFE. In particular, the polar component results from these different intermolecular forces due to permanent and induced dipoles and hydrogen bonding, whereas the dispersive component of surface free energy is due to instantaneous dipole moments, like the Coulomb interaction between an electron and the nuclei in two molecules.¹⁵⁾

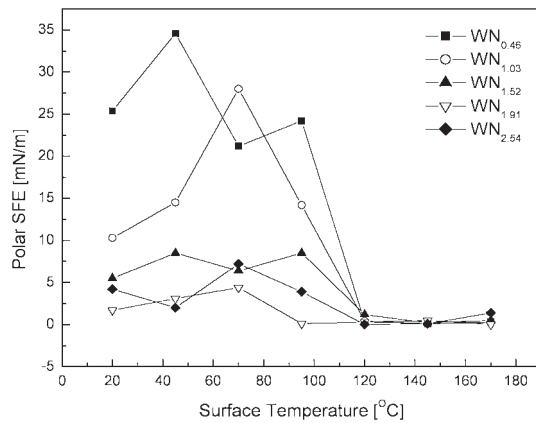
Figure 2 shows the effect of different composition on the total surface free energy (SFE) and the SFE components of WN_x films at 20°C surface temperature calculated using the Owens-Wendt geometric mean approach in Table 2. When the composition was in the WN_{0.46}–WN_{2.54} range, it influenced the total SFE, dispersive SFE and polar SFE of the WN_x films. It is interesting to find that a low surface free energy coating is needed to meet the ever increasing demands in IC package molding industries. In this study, the total SFE at 20°C decrease with N₂ content to raise to 37.6 mN/m (WN_{1.91}) at the start, and then increase. In general, one can say that a larger contact angle value implies a lower SFE. Because a larger contact angle means that a weaker hydrogen bonding, resulting in a lower SFE. The polar SFE component has same trend with total SFE, but the dispersive SFE component is on the contrary exactly. The polar SFE component is also lower than the dispersive SFE component. This is resulting from hydrogen bonding being polar. In reality, the actual SFE is affected by many factors including deposition parameters, composition, temperature, roughness,



(a)



(b)



(c)

Fig. 3 Effect of surface temperature on the surface free energy components of WN_x thin films prepared at different composition. (a) Total SFE; (b) Dispersive SFE; (c) Polar SFE.

element, etc. However, The above results with surface free energy calculation clearly point out the correlation between SFE and composition.

3.4 Effect of temperature on the surface free energy of WN_x films

Figures 3(a), 3(b), and 3(c) show the surface temperature effects on the total SFE, dispersive SFE and polar SFE of WN_x films prepared at different composition. The result indicated that the SFE film components decreased with

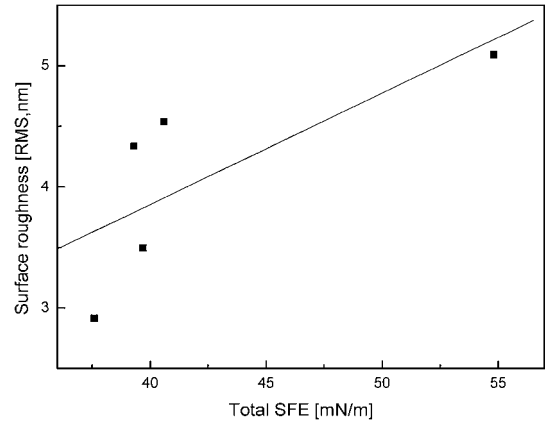


Fig. 4 Relationship between surface free energy and surface roughness.

increasing surface temperature. This is because water, Diiodomethane and Ethylene glycol are known to have hydrogen atoms, leading to hydrogen bonding. Hydrogen bonds give WN_x film high surface free energy, making it behave as though it were coated with an invisible film (solid-liquid interface). When surface of WN_x film is heated, the heat energy first disrupts the hydrogen bonds and then makes the liquid molecules move faster and vaporize gradually. Conversely, when liquids are cooled, more hydrogen bonds form and the WN_x films have high surface free energy. Another reason is that surface free energy γ_s can be expressed as a function of the surface internal energy U_s , temperature T , and surface entropy, S_s :¹⁶⁾

$$\gamma_s = U_s - TS_s, \quad (8)$$

As S_s increases with increasing temperature, the surface free energy γ_s decreases with increasing temperature according to the above equation. For semiconductor IC packaging molding applications, creating a higher temperature environment will decrease the EMC surface sticking effect on packaging dies.

3.5 Relationship between roughness and surface free energy

The surface of SFE samples were investigated in a nano-scale area by an atomic force microscope (AFM) using a silicon tip as a probe.¹⁷⁾ The AFM physical principle is based on the interaction between the probe tip and surface. When the cantilever tip approaches the sample surface the Van der Waals Force starts acting upon it. A constant oscillation amplitude is maintained by maintaining the same signal level proportional to the oscillation amplitude. This signal indicates the degree of roughness (RMS).

The relation between the surface free energy and surface roughness was shown in Fig. 4. The SFE was calculated using the contact angle test at 20°C and surface roughness standard deviation was in the height values with a given AFM image area. It showed that there is a linear increased SFE tendency with increasing surface roughness. The linear increased SFE tendency with increasing surface roughness is due to that the SFE γ_s can be expressed as a function of the adhesion constant force F_c at the AFM tip and surface roughness R_{rms} (RMS):^{17,18)}

$$\gamma_s = W = \frac{1}{N} \sum_i^N \vec{F}_i \cdot \vec{r}_i = \frac{1}{N} \vec{F}_C \cdot \sum_i^N \vec{r}_i \sim F_c R_{rms} \quad (9)$$

Where γ_s is the average work W done by the adhesion force vector \vec{F}_i on the surface as the tip of AFM moves the displacement vector \vec{r}_i . The adhesion force (F_i) was indicated by multiplying the height using the spring constant of the tip. The tip height (RMS) measurement just before release from contact with the sample surface. We summed the work increments for various points. N is the number of samples. The surface free energy γ_s increases with increasing surface roughness according to the above equation.

4. Conclusion

The surface free energy of WN_x films deposited by RF sputter was investigated. The important conclusions are as follows.

- (1) With raising N₂ content, the contact angle at 20°C go up to 116.7° at beginning, corresponding to WN_{1.91}, and then drop off. In addition, the contact angle components decreased with increasing surface temperature. Because increasing surface temperature disrupts the hydrogen bonds between water, Diiodomethane, Ethylene glycol and the films and liquids vaporize gradually.
- (2) The variation in the surface free energy of WN_x films depends on various composition. The total SFE at 20°C decrease with N₂ content to raise to 37.6 mN/m(WN_{1.91}) at the start, and then increase. Because a larger contact angle means that a weaker hydrogen bonding, resulting in a lower SFE. The polar SFE component has same trend with total SFE, but the dispersive SFE component is on the contrary exactly. The polar SFE component is also lower than the dispersive SFE component. This is resulting from hydrogen bonding being polar. With increasing surface temperature, the surface free energy WN_x components decreased. This is because water, Diiodomethane and Ethylene glycol evaporation on the surface, disrupted hydrogen bonds and surface entropy increasing with increasing temperature.
- (3) The RMS roughness effects the surface free energy. There is tendency for the SFE to increase with increasing surface roughness in WN_x films. Because

SFE and surface roughness can be expressed as a function in direct ratio.

- (4) The data on the surface free energy of WN_x films at different temperatures will contribute to injection molding industrial equipment operation and design, especially, in semiconductor IC packaging molding applications.

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