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Cu films prepared by bipolar pulsed high power impulse magnetron sputtering

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ABSTRACT

Bipolar pulse High Power Impulse Magnetron Sputtering (HiPIMS) based on conventional HiPIMS is put forward to deposit Cu films on silicon wafers. Positive kick pulses with different pulse width and magnitude are applied after the initial negative pulse to drive Cu ions to the substrate, improving the properties of Cu films. Compared to films deposited by conventional HiPIMS, the Cu films prepared by modified HiPIMS exhibit a higher deposition rate. And the increase in voltage and pulse width of kick pulse results in a reduction of tensile stress of the Cu films. The bipolar pulse HiPIMS has potential applications in Cu metallization for semiconductor processing and other applications.

1. Introduction

Copper has been proposed as a metallization material for Ultra Large-Scale Integration (ULSI) because of its high chemical stability, low resistivity, and excellent electromigration resistance [1,2]. Large differences in the physical and chemical properties between Cu and Si lead to poor film adhesion, low density, and sensitivity to oxidation [3,4]. As a promising physical vapor deposition (PVD) technology, high power impulse magnetron sputtering (HiPIMS) has been used for Cu metallization in recent years [5–10]. It usually applies a high power density (several kW/cm^2) at a low duty cycle. High plasma densities (up to 10^{19} m^{-3}) can be obtained, resulting in a high ionization rate of target materials [10]. These ionized atoms have much higher energies than sputtered atoms in conventional direct current magnetron sputtering (DCMS), and the films prepared by HiPIMS tend to be smooth and dense [11–13].

It is found that Cu films prepared by HiPIMS exhibit a larger grain size and less boundary density [5–7]. The films show much smaller resistivity and better oxidation resistance compared to those deposited by DCMS. However, it suffers from a large drawback that the deposition rate is lower than that of DCMS for the same average power. The most common explanation is that the highly ionized meal atoms are attracted back to the target [14–16]. Meanwhile, the magnetic confinement of the metal ions also leads to the reduction the deposition rate [17]. It means that the metal ionization rate around the substrate is relative lower than that in front of target, weakening the advantage of HiPIMS.

In the study of pulsed-DC, it is reported that the use of positive reversed voltage can raises the potential of after-glow plasma compared to grounded chamber walls (including substrates), resulting in the increase of the incident energy of ions to the substrate [18,19]. So the growing films structure, deposition rate and other properties can be improved significantly [20–22]. In Takeo's study [23], the positive reversed pulse was also put forward in conventional HiPIMS. A positive 100 V voltage was applied in the whole pulse-off time, aiming at driving the metal ions to the substrate. However, few report were found concerning the properties of films grown by this new high power bipolar pulsed magnetron sputtering. Meanwhile, the magnitude and the pulse width of the reverse pulse are the key parameters, which are closely related to films properties. Therefore, in order to improve the ion deposition

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rate while improving the Cu films properties, the Cu films were prepare by the new bipolar pulse high power magnetron sputtering based on the conventional HiPIMS. A positive kick voltage is applied after initial pulse, and the magnitude and the pulse width of the reverse pulse can be controlled as you want. The effect of bipolar pulse on the Cu films properties is studied in detail.

2. Experiment details

The experimental vacuum chamber is evacuated to a base pressure of 6.7×10^{-3} Pa with a pure (99.99%) linear Cu target (254×127 mm^2), positioned 101.6 mm (4 inches) from the substrate. The TriPack magnetic field configuration was used to generate more metal ions for all the experiments, which is well described for a circular pack by Raman et al. [9,17]. and in McLain [24] for a rectangular pack. Five p-type (100) silicon wafers were fixed on the substrate. High purity argon gas was introduced using a mass flow controller. The deposition pressure was controlled at 1.1 Pa (8×10^{-3} Torr) during deposition. There is no heating and bias during deposition. All the samples were vented at room temperature after about 120 min exposure.

HiPIMS power consisted of a DC power supply (Magna-Power Electrons, XR-4) and impulse power supply (Starfire Industries, Impulse 2-2) was used to power the magnetrons. During experiments, a typical set of discharge parameters consisted of a voltage of 710 V, a pulse width of 100 μs, and a frequency of 600 Hz, and the positive kick pulse with varying voltages and pulse widths was applied after the initial pulse with a delay time of 4 μs between bipolar pulses. A DC power supply (Advanced Energy, Pinnacle Series) was also used independently to power the magnetrons for comparison at same avergae power. The detailed parameters were shown in Table 1.

During sputtering, the target current I(t) and voltage V(t) were measured by a oscilloscope (Tektronix, TPS 2024B) with a current sensor (Honeywell, CSNK591) and a voltage probe (Tektronix, model P-5100), respectively. The film thickness and surface profiles were measured using a Dektak-3 stylus profilometer. And the deposition rate is the ratio between the measured thickness and the deposition time, and it is expressed in nm/min. The deformed profile was scanned along the length direction on the length/width ratio (3:1) of the wafer [25], which was used calculate the film stress with the Stoney equation [26]. The surface topography were characterized using a filed-emission scanning electron microscopy (FE-SEM) (JEOL, JSM-7000F).

3. Results and discussions

Fig. 1 shows the HiPIMS VI (Voltage-Current) waveform of the Cu target. The shapes of all the target voltage are square pulse. After the onset of pulse, the discharge current increases rapidly to the maximum value approximately 40 A at the end of the initial pulse, and then drops to zero within 2 μs. Although the peak current is only 40 A, the peak electron density was measured to be 1–3 *10^{19}/m^3 at 0.5 inch away from the Cu target surface [24]. When the kick pulse is applied, a positive pulse with varying voltages and pulse widths can be observed after the initial pulse with no noticeable effect in discharge current. Fig. 2 shows the plasma during deposition. It is found that three racetracks are present on the surface. In DCMS operation, the color of plasma is deep blue and purple, indicating that the Ar ions and Cu atom dominate the species. But in HiPIMS operation, the color of plasma is green. That means the plasma becomes dominated by the Cu ions. It is interesting to see that the green appears dimmer when applying the positive kick pulse, which could be explained by the plasma being pushed away from the target.

Table 1
Experimental parameters during deposition.

Power Supply	Parameters	Kick pulse (pulse width, Voltage)	Average power
DCMS	503 V, 1.96 A	No	986 W
Conventional HiPIMS	710 V, 600 Hz, 100 μs	No	1032 W
Modified HiPIMS	710 V, 600 Hz, 100 μs	100 μs, 50 V	1032 W
Modified HiPIMS	710 V, 600 Hz, 100 μs	100 μs, 150 V	996 W
Modified HiPIMS	710 V, 600 Hz, 100 μs	500 μs, 50 V	1032 W

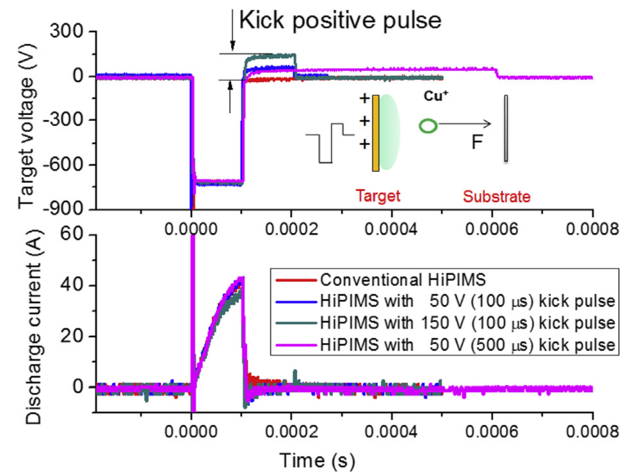

Fig. 1. Voltage and current of the target from Starfire Impulse power supply for TriPack Linear Cu target at 8 mTorr and 1000 W average power.

The effect of the kick pulse on the properties of the Cu films is studied further. The deposition rate of the Cu films across the center-line length of Cu target is shown in Fig. 3. The data was taken across half of the target and mirrored onto the other half for visual simplicity. As usual, the deposition rate of Cu films deposited by HiPIMS is lower than the one deposited by DCMS. This is due to several reasons [14–16], such as the return effect where ionized sputtered material returns to the target, the yield effect, and power loss in the switch module. When the kick pulse is applied, an increase in deposition rate was observed for all cases. The bar graph in Fig. 3 shows the average value of all deposition rates for all the samples at different positions. It is also found that the increase of voltage and pulse width of the kick pulse can improve the deposition rate further.

Fig. 4 shows the surface topography of Cu films prepared by different methods. The Cu films deposited by DCMS shows small globular microstructures with grain sizes of approximately 40 nm. Due to the highly ionized deposition flux of HiPIMS, the films exhibit larger grain size and less boundary density. In the case of HiPIMS with kick pulse (Fig. 4 c, e), it is noted that the grain boundaries are difficult to identify, small grains gather together when the kick pulse is applied, indicating the growth of “zone-T” regions [27,28]. In the case of the kick pulse, it is hard to see obvious grain boundaries, potentially indicating the presence of a high ion flux onto the substrate [27]. Meanwhile, the kick pulse will increase the potential difference between the target and substrate, resulting in a more effective bombardment of positive ions on the films. The grains become finer and the film surface appeared significantly flattened, though RMS roughness measured by an AFM showed little overall difference.

The residual stress is closely related to the films quality, which is generally recognized in Cu metallization. Excessive residual

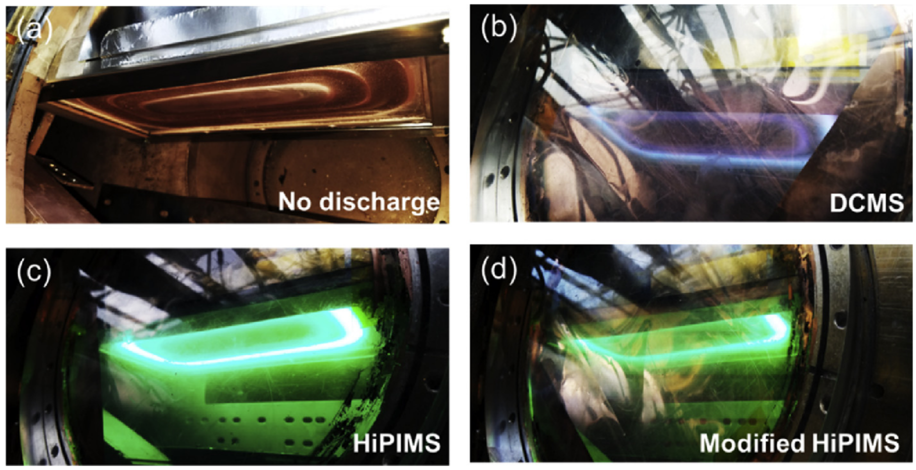

Fig. 2. Plasma during TriPack with a Cu target in operation (a) no discharge; (b) DCMS; (c) HiPIMS; (d) Modified HiPIMS with 50 V (100 µs) kick pulse. The color of plasma is deep blue and purple in DCMS operation, the color of plasma is green in HiPIMS operation, and green appears dimmer in the modified HiPIMS. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

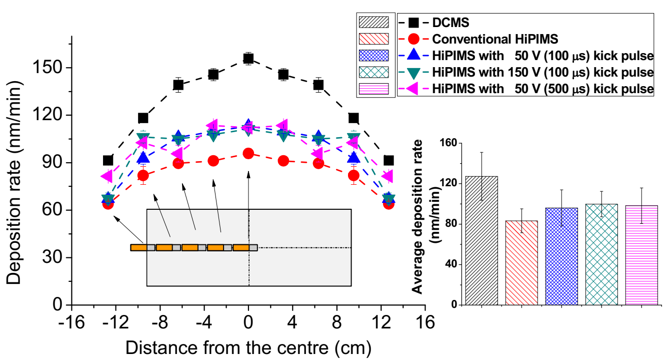

Fig. 3. Deposition rate of Cu films across the center-line length of Cu target. Average deposition rate is the average value of deposition rate of all the samples at different position.

stresses in thin films may cause defect formation and delamination at the film–substrate interface, leading to decrease of the stability and reliability of the components and devices. Therefore, it is significant to tailor the residual stress. Fig. 5 a and b show the deformation profiles of Si following the Cu deposition. Because of the significant mismatch in thermal expansion coefficient between the Cu films and Si substrate [6], all the Cu films exhibit tensile stress, as shown in Fig. 5 (a). The films prepared by modified HiPIMS have smaller deformation than that prepared by conventional HiPIMS. It means the kick pulse can reduce the tensile stress effectively.

Further, the residual stress values at different positions were calculated with Stony's equation, as shown in Fig. 5c. It is noted that the stress of Cu films prepared by conventional HiPIMS is much larger than the one deposited by DCMS. This could be explained that grain growth (Fig. 4d) generally makes the film more tensile due to the coalescing of the boundaries. Stress data for the sample which was ~100 mm from the center was not obtained due to the films peeling off. This is likely due to a large residual stress. In the case of the HiPIMS with kick pulse, the kick pulse could repel more ions to the substrate, resulting in the ionization rate increasing. Future work will measure the ion flux fraction directly as well as the downstream plasma parameters. Generally when a film is deposited under energetic particle bombardment, the extensive amount of ion flux and the higher ion energies cause the finer grains and denser films to be formed, resulting in a substantial decrease of tensile stress. Meanwhile, more ion bombardment will result in surface diffusion, local heating, collapse of voids, and recrystallization, which also contributes to the decrease of tensile stress [29].

Based on the actual conditions, we estimated the flux increase as follows. Fig. 6 is a schematic for discharge region in our experiment for the magnetron (Grey – sputtering target, Red – Plasma volume, Golden – expansion surface available for plasma).

Plasma volume is considered above racetrack and is ~25 mm thick.

$$\mathrm{Volume_{plasma}} \approx 500\ [\mathrm{cm^3}]$$

The density of the plasma in front of the target has been measured [24] at $3*10^{13}$ [ions/cm^3]. Since this is the end of a HIPIMS plasma where the recirculating ion flux is a maximum, we assume all of those ions are target species. Therfore the amount of stored target ions in the plasma volume at the end of the pulse is:

$$\mathrm{N_{total}} = \mathrm{n_{plasma}} * \mathrm{Volume_{plasma}} = 3*10^{13}\ [\mathrm{ions/cm^3}] * 500\ [\mathrm{cm^3}] = 1.5*10^{16}\ [\mathrm{ions}]$$

The total expansion surface (S_{exp}) 100 mm away from the target (where substrate is located) and the area of target are shown as follows,

$$S_{exp} = 1818\ [\mathrm{cm^2}] \approx 1800\ [\mathrm{cm^2}]$$

$$S_{traget} = 322\ [\mathrm{cm^2}]$$

Assumption 1. If all ions from plasma volume homogenously spread on all over available surface. (No recombination, no directional inhomogeneity, no effects from magnetic/electric fields).

Total amount of ions per cm^2:

$$T_{ions\ homo} = \frac{N_{total}}{S_{exp} + S_{target}} = \frac{1.5*10^{16}[ions]}{1800 + 322\ [cm^2]} \approx 7*10^{12}\left[\frac{ions}{cm^2}\right]$$

Total amount of ions which go towards the target:

$$N_{ions\ on\ target} = T_{ions\ homo} * S_{target} = 7*10^{12}\left[cm^{-2}\right]*322\ \left[cm^2\right] \approx 2.3*10^{15}\ [\mathrm{ions}]$$

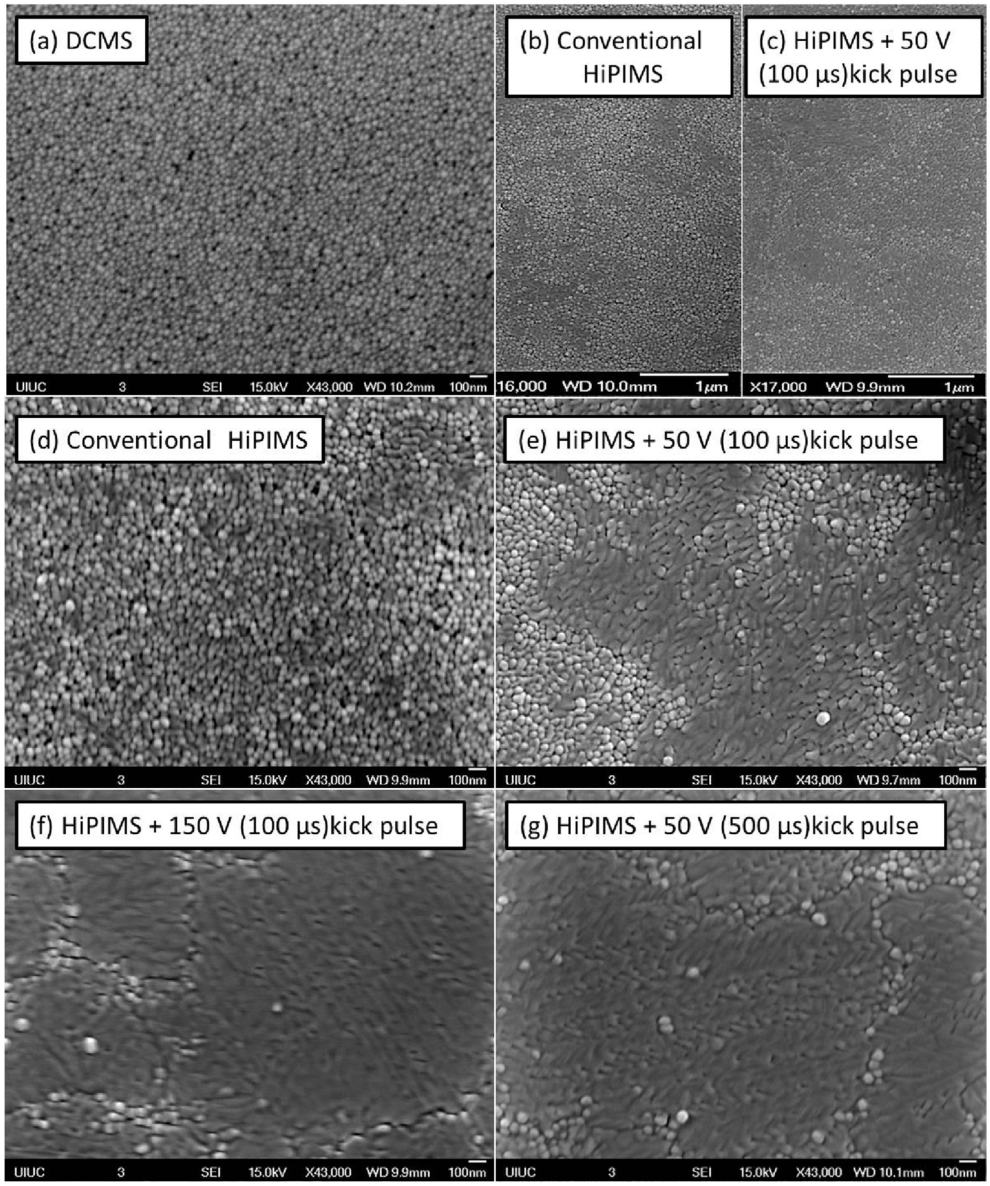

Fig. 4. The SEM images of Cu films prepared by different methods.

Assumption 2. If we add positive kick, only ions which go towards the target will be affected and will be reflected from target.

The number of ions which will be added to the ion flux towards substrate if ions (which go towards the target) are reflected from the target during positive kick:

$$T_{ions\ add\ on} = \frac{N_{ions\ on\ traget}}{S_{exp}} = \frac{2.3*10^{15}[ions]}{1800\ [cm^2]} \approx 1.3*10^{12}\left[\frac{ions}{cm^2}\right]$$

$$Increase\ in\ flux = \frac{T_{ions\ addon}}{T_{ions\ homo}}*100[\%] = \frac{1.3*10^{11}\left[\frac{ions}{cm^2}\right]}{7*10^{12}\left[\frac{ions}{cm^2}\right]}*100 \approx 18.6\%$$

According to the data of actual deposition rate, deposition rate at the center position is 95 nm/min in the case of conventional HiPIMS. And the deposition rate is 113 nm/min when the kick pulse is applied.

So the increase in deposition rate (Increase in dep),

Increase in dep = 113/95−1 = 18.9%,

This is consistent with the results of estimation.

4. Conclusions

A new bipolar pulse high power impulse magnetron sputtering (HiPIMS) system to prepare Cu films on Si is explored. A positive kick pulse is applied to the target after the initial negative pulse to drive more metal ions to substrate. Compared to films deposited by conventional HiPIMS, the new approach can improve the deposition rate effectively, reducing the residual tensile stress between film and substrate. These could be further beneficial for improving the Cu films properties, such as electronic conductivity and adhesion, indicating the potential applications of HiPIMS to Cu metallization in semiconductor processing.

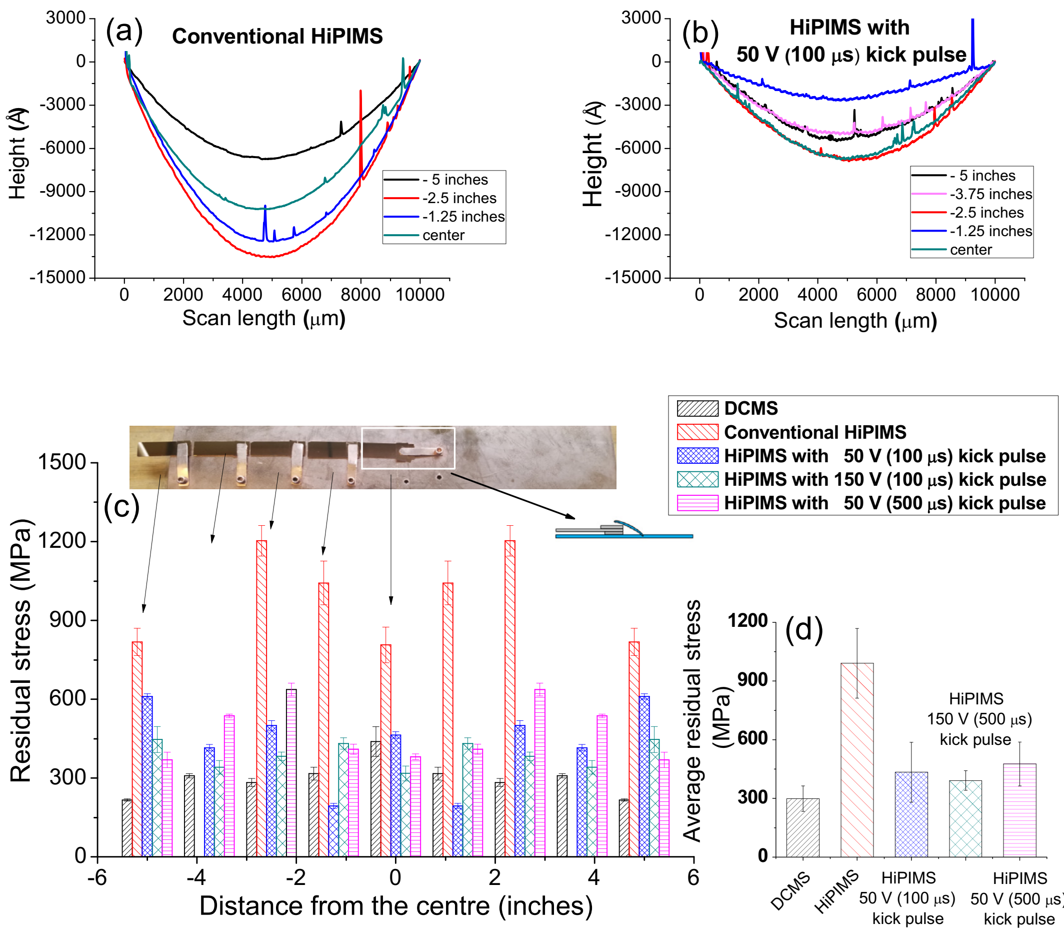

Fig. 5. (a) (b) Deformation profiles of Si substrates following Cu films depositon at different position and (c) (d) residual stress of Cu films calculated with Stoney's equation.

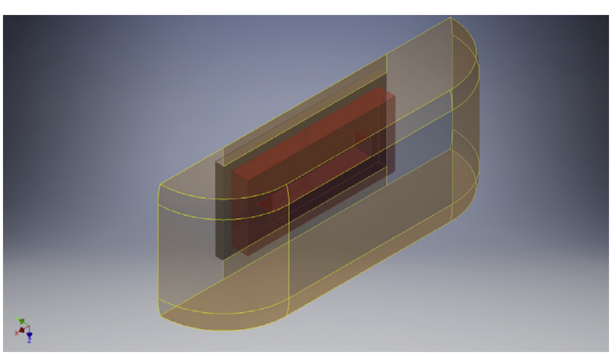

Fig. 6. Schematics for discharge region in our experiment for 254*127 mm^2 magnetron. Grey – sputtering target, Red – Plasma volume, Golden – expansion surface available for plasma at the target-to-substrate distance. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

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References

[1] M. Yu, J. Zhang, D. Li, Q. Meng, W. Li, Internal stress and adhesion of Cu film/Si prepared by both MEVVA and IBAD, Surf. Coating. Technol. 201 (2006) 1243–1249.

[2] S. Gandikota, S. Voss, R. Tao, A. Duboust, Dennis Cong, L.-Y. Chen, et al., Adhesion studies of CVD copper metallization, Microelectron. Eng. 50 (2000) 547–553.

[3] H. Ron, H. Cohen, S. Matlis, M. Rappaport, I. Rubinstein, Self-assembled monolayers on oxidized metals. 4. Superiorn-alkanethiol monolayers on copper, J. Phys. Chem. B 102 (1998) 9861–9869.

[4] L. Chen, Q. Wang, J. Cai, G. Ma, Y. Hu, T. Lee, Study of glass metallization and adhesion evaluation for TGV application Electronic Packaging Technology (ICEPT), in: 14th International Conference on 2013, 2013, pp. 217–220.

[5] A.A. Solovyev, V.A. Semenov, V.O. Oskirko, K.V. Oskomov, A.N. Zakharov, S.V. Rabotkin, Properties of ultra-thin Cu films grown by high power pulsed magnetron sputtering, Thin Solid Films 631 (2017) 72–79.

[6] B.H. Wu, J. Wu, F. Jiang, D.L. Ma, C.Z. Chen, H. Sun, et al., Plasma characteristics and properties of Cu films prepared by high power pulsed magnetron sputtering, Vacuum 135 (2017) 93–100.

[7] F. Cemin, D. Lundin, D. Cammilleri, T. Maroutian, P. Lecoeur, T. Minea, Low electrical resistivity in thin and ultrathin copper layers grown by high power impulse magnetron sputtering, J. Vac. Sci. Technol.: Vac., Surf., Films 34 (2016), 051506.

[8] L. Meng, H. Yu, J.R. Sporre, P. Raman, M.M. Szott, J.T. McLain, et al., Direct measurement and modeling of the redirected ion flux in a high-powered pulsed-plasma magnetron, J. Vac. Sci. Technol.: Vac., Surf., Films 33 (2015), 031301.

[9] P. Raman, J. Weberski, M. Cheng, I. Shchelkanov, D.N. Ruzic, A high power impulse magnetron sputtering model to explain high deposition rate magnetic field configurations, J. Appl. Phys. 120 (2016) 163301.

[10] V. Kouznetsov, K. Macák, J.M. Schneider, U. Helmersson, I. Petrov, A novel pulsed magnetron sputter technique utilizing very high target power densities, Surf. Coating. Technol. 122 (1999) 290–293.

[11] G. Greczynski, J. Böhlmark, Y.T. Pei, C.Q. Chen, J.T.M.D. Hosson, M. Alunovic, et al., High power impulse magnetron sputtering for industrial applications:

deposition of chromium films on inclined surfaces, in: 51st Annual Technical Conference Proceedings, 2008, pp. 282–287. Chicago.
[12] G. Greczynski, J. Lu, J. Jensen, S. Bolz, W. Kölker, C. Schiffers, et al., A review of metal-ion-flux-controlled growth of metastable TiAlN by HIPIMS/DCMS co-sputtering, Surf. Coating. Technol. 257 (2014) 15–25.
[13] D. Lundin, K. Sarakinos, An introduction to thin film processing using high-power impulse magnetron sputtering, J. Mater. Res. 27 (2012) 780–792.
[14] D.J. Christie, Target material pathways model for high power pulsed magnetron sputtering, J. Vac. Sci. Technol.: Vac., Surf., Films 23 (2005) 330.
[15] G. Greczynski, L. Hultman, Peak amplitude of target current determines deposition rate loss during high power pulsed magnetron sputtering, Vacuum 124 (2016) 1–4.
[16] A. Andre, Deposition rates of high power impulse magnetron sputtering: physics and economics, J. Vac. Sci. Technol.: Vac., Surf., Films 28 (2010) 783.
[17] P. Raman, I.A. Shchelkanov, J. McLain, D.N. Ruzic, High power pulsed magnetron sputtering: a method to increase deposition rate, J. Vac. Sci. Technol.: Vac., Surf., Films 33 (2015), 031304.
[18] M. Čada, J.W. Bradley, G.C.B. Clarke, P.J. Kelly, Measurement of energy transfer at an isolated substrate in a pulsed dc magnetron discharge, J. Appl. Phys. 102 (2007), 063301.
[19] S.K. Karkari, A. Vetushka, J.W. Bradley, Measurement of the plasma potential adjacent to the substrate in a midfrequency bipolar pulsed magnetron, J. Vac. Sci. Technol.: Vac., Surf., Films 21 (2003) L28–L32.
[20] C. Corbella, E. Pascual, M.A. Gómez, M.C. Polo, J. García-Céspedes, J.L. Andújar, et al., Characterization of diamond-like carbon thin films produced by pulsed-DC low pressure plasma monitored by a Langmuir probe in time-resolved mode, Diam. Relat. Mater. 14 (2005) 1062–1066.
[21] M. Rubio-Roy, C. Corbella, J. Garcia-Céspedes, M.C. Polo, E. Pascual, J.L. Andújar, et al., Diamond like carbon films deposited from graphite target by asymmetric bipolar pulsed-DC magnetron sputtering, Diam. Relat. Mater. 16 (2007) 1286–1290.
[22] H.C. Barshilia, K.S. Rajam, Reactive sputtering of hard nitride coatings using asymmetric-bipolar pulsed DC generator, Surf. Coating. Technol. 201 (2006) 1827–1835.
[23] T. Nakano, C. Murata, S. Baba, Effect of the target bias voltage during off-pulse period on the impulse magnetron sputtering, Vacuum 84 (2010) 1368–1371.
[24] J. McLain, Linear Magnetron High Deposition Rate magnet Pack for High Power Impulse Magnetron Sputtering, M, Dept. of Nuclear, Plasma and Radiological Engineering, University of Illinois at Urbana-Champaign, 2016. S Thesis.
[25] F. Jiang, S. Chen, Y. Leng, N. Huang, Effect of wafer size on the film internal stress measurement by wafer curvature method, J. Wuhan Univ. Technol.-Mater. Sci. 31 (2016) 93–99.
[26] G.G. Stoney, The tension of metallic films deposited by electrolysis. Proceedings of the royal society of london a: mathematical, Phys. Eng. Sci. 82 (1909) 172–175.
[27] A. Anders, A structure zone diagram including plasma-based deposition and ion etching, Thin Solid Films 518 (2010) 4087–4090.
[28] F.C.M. van de Pol, F.R. Blom, T.J.A. Popma, R.f. planar magnetron sputtered ZnO films I: structural properties, Thin Solid Films 204 (1991) 349–364.
[29] Y.H. Cheng, B.K. Tay, S.P. Lau, X. Shi, H.S. Tan, Influence of substrate bias on the microstructure and internal stress in Cu films deposited by filtered cathodic vacuum arc, J. Vac. Sci. Technol.: Vac., Surf., Films 19 (2001) 2102.