Low temperature growth of stress-free single phase $\alpha$-W films using HiPIMS with synchronized pulsed substrate bias

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Low temperature growth of stress-free single phase $\alpha$-W films using HiPIMS with synchronized pulsed substrate bias

ABSTRACT
Efficient metal-ion-irradiation during film growth with the concurrent reduction of gas-ion-irradiation is realized for high power impulse magnetron sputtering by the use of a synchronized, but delayed, pulsed substrate bias. In this way, the growth of stress-free, single phase $\alpha$-W thin films is demonstrated without additional substrate heating or post-annealing. By synchronizing the pulsed substrate bias to the metal-ion rich portion of the discharge, tungsten films with a $\langle 110 \rangle$ oriented crystal texture are obtained as compared to the $\langle 111 \rangle$ orientation obtained using a continuous substrate bias. At the same time, a reduction of Ar incorporation in the films are observed, resulting in the decrease of compressive film stress from $\sigma = 1.80$–1.43 GPa when switching from continuous to synchronized bias. This trend is further enhanced by the increase of the synchronized bias voltage, whereby a much lower compressive stress $\sigma = 0.71$ GPa is obtained at $U_s = 200$ V. In addition, switching the inert gas from Ar to Kr has led to fully relaxed, low tensile stress (0.03 GPa) tungsten films with no measurable concentration of trapped gas atoms. Room-temperature electrical resistivity is correlated with the microstructural properties, showing lower resistivities for higher $U_s$ and having the lowest resistivity (14.2 $\mu\Omega$ cm) for the Kr sputtered tungsten films. These results illustrate the clear benefit of utilizing selective metal-ion-irradiation during film growth as an effective pathway to minimize the compressive stress induced by high-energetic gas ions/neutrals during low temperature growth of high melting temperature materials.

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I. INTRODUCTION
Tungsten (W) thin films are receiving a great amount of attention for many different industrial applications due to their refractory properties such as high physical stability and chemical inertness. In particular, the equilibrium $\alpha$-W bcc tungsten, has attractive properties like the highest melting temperature ($T_m = 3422$ °C) and the lowest thermal expansion coefficient (4.5 $\times$ 10$^{-6}$ K$^{-1}$) among metals, together with a low electrical resistivity (5.28 $\mu\Omega$ cm). From a mechanical point of view, it exhibits considerable hardness and toughness at high temperatures. These unique features has led to its use in the metallization of integrated circuits as contact plugs and as diffusion barriers. Tungsten has also been considered for use in x-ray reflection masks and as electrode material for high-temperature surface acoustic wave devices. Nanostructured tungsten films are also interesting as a protective coating. Its high density (19.3 g/cm$^3$), low sputtering yield, and low coefficient of electron emission also make tungsten a candidate for the primary plasma-facing materials in fusion reactors. Recently, a metastable form of tungsten ($\beta$-W with the A15 cubic structure) was found to be a good candidate for spin–orbit torque applications due to its large spin Hall angle and high resistivity (150–350 $\mu\Omega$ cm). However, $\beta$-W also shows a high tensile stress that occurs due to the
phase transformation to α-W that occurs at moderate temperatures, making it unsuitable for many applications.\(^{15}\)

To avoid the formation of β-W and to obtain primary α-W, a sufficiently high surface mobility needs to be maintained during film growth.\(^{16}\) At low growth temperatures, a route to increase surface mobility is to apply momentum transfer from particles impinging the growing film.\(^{16}\) Monte Carlo simulations have shown that for a relatively low working gas pressure of \(\sim 0.2\) Pa, the average kinetic energy of sputtered tungsten is as high as \(20\) eV.\(^{17}\) This energy is sufficient to enhance the surface mobility of tungsten to overcome the surface diffusion barrier leading to crystalline growth of the α-W phase.\(^{18},^{19}\) However, bombardment by high-energy sputtering gas atoms/ions can cause film stress due to the incorporation of excess atoms in the film.\(^{19}\) Most of the previously reported primary α-W films, with thicknesses above \(50\) nm, show compressive in-plane stress in the range of \(3–7\) GPa.\(^{20}\) This will limit the thickness of tungsten films to \(\sim 150\) nm due to film failure.\(^{20}\) These deleterious effects can be minimized by optimizing the energy of impinging particles, mainly ions, to below that of the bulk lattice displacement threshold. In early studies by Kao et al.,\(^{21}\) compressive stress was significantly reduced from \(4.8\) to \(1\) GPa by increasing the flux of Ar ions with energy of \(100–150\) eV. However, Ar entrapment in interstitial sites could not be completely suppressed and thus the zero-stress condition was not achieved.

To overcome the issue with compressive stress induced by rare gas incorporation in the films, an alternative way is to efficiently irradiate with metal ions of the growth material.\(^{22}\) This can be achieved by using ionized-PVD, such as high power impulse magnetron sputtering (HiPIMS).\(^{23}\) Key features of HiPIMS are (1) ionization of a large fraction of the sputtered metal flux and (2) time separation between metal- and gas-ion fluxes incident at the substrate.\(^{24}\) In the recent reports by Velicu et al.\(^{26}\) and Engwall et al.,\(^{27}\) a clear advantage of utilizing HiPIMS has been demonstrated in the growth of dense tungsten coatings with film thickness between \(400\) and \(1200\) nm, respectively. The films, however, contained compressive stress of \(\sim 2\) GPa. The second feature of HiPIMS (time separation of ion arrivals to the substrate) enables the further precise selective tuning of metal-ion energy and momentum transfer during the film growth without introducing film stresses through minimizing the incorporation of gas ions by synchronizing the pulsed substrate bias with the metal-rich portion of HiPIMS pulses. This was first demonstrated by Grechynski et al.\(^{28}\) showing film densification, microstructure enhancement, surface smoothing, and decreased film stress with no measurable Ar incorporation in Ti\(_x\)Al\(_{1-x}\)N films. Significant enhancement of surface mobility by efficient metal-ion-irradiation was demonstrated also by the deposition of the high melting temperature material Hf (\(T_m \sim 2233\) °C) on unheated substrates, showing epitaxial growth of HfN thin films on MgO(001) at very low \(T_b\) (<0.10).\(^{28}\)

To clarify the impact of metal-ion-irradiation during film growth, and at the same time, the reduction of gas atoms and gas-ion-irradiation, the present work investigates the low temperature growth of tungsten films by the use of a synchronized pulsed substrate bias in HiPIMS discharges. The synchronization of the negative substrate bias pulse with the metal-rich portion of the HiPIMS discharges were selected based on the time evolution of the ion fluxes in the pulsed sputtering process, as investigated by optical emission spectroscopy (OES) and ion mass spectrometry. The effect of the nature of the incident ions, gas vs metal ions, and their energies have been studied by comparing tungsten film growth in argon (Ar) discharges under different substrate bias configurations; continuously applied bias and synchronized pulsed bias with negative bias voltage \(U_b\) values ranging between \(50\) and \(200\) V. The effect of reducing the number back-reflected Ar gas atom was also explored by using krypton (Kr) as an alternative working gas.

II. EXPERIMENTAL

All experiments were performed in a high vacuum stainless-steel chamber with a base pressure of \(\sim 10^{-8}\) Pa. A planar circular unbalanced magnetron with a tungsten (99.999% in purity) disk with a diameter of \(75\) mm and a thickness of \(5\) mm was used as the sputtering target. Ar or Kr gas with a purity of 99.997% was introduced into the chamber through a mass-flow controller at a constant flow rate of \(100\) sccm and was maintained at a constant working pressure of \(1.0\) Pa by adjusting the pumping speed via the main gate valve.

Unipolar HiPIMS pulses, \(100\) μs in length, were supplied by a HiPSTER 1 pulsing unit fed by a 1 kW HiPSTER 1-DCPSU DC power supply (Iontastics AB, Sweden). The pulse frequency was adjusted in the range of \(100–150\) Hz to maintain an average power in the range of \(250–280\) W. The target current and voltage characteristics were recorded and monitored with a Tektronix TBS 2104 digital oscilloscope connected directly to the HiPSTER pulsing unit.

To analyze the time evolution of HiPIMS discharges in a Ar atmosphere, especially the development of the plasma composition close to the target, time-resolved optical emission spectroscopy (OES) was performed using an optical monochromator system MS3501i (SOL Instruments Ltd.) with a grating of line density of \(12001/mm\) (which has an optical resolution of \(0.06\) nm) operating with an intensified-CCD photodetector, iStar ICCD DH320T (Andor Technology Ltd.). The emission spectra were collected through a collimator quartz lens with an aperture of \(9.5\) mm and a quartz optical fiber capable of transmitting in the ultraviolet spectral region, mounted in the deposition chamber with the line of sight parallel with and \(25\) mm from the target surface. To obtain the temporal evolution of neutral and ionized species in the plasma composition at a given set of discharge conditions, representative emission lines were carefully selected based on their intensity, excitation energy, and transition probability. Table 1 summarizes a list of selected Ar I, Ar II, W I, and W II lines with details of the excitation and transition of these lines.\(^{29}\)

To obtain the time evolution of the selected line intensities during HiPIMS discharges, the ICCD camera was triggered synchronously with the HiPIMS pulsing unit with a gate width of \(3\) μs. The delay time with respect to the onset of the voltage pulse to the cathode varied up to \(120\) μs in \(4\) μs intervals. The signal-to-noise ratio was optimized by accumulating the spectra acquired during 100 consecutive pulses for each time point.

In situ time-dependent mass and energy analyses of the ion flux incident at the substrate plane were carried out using a Hiden Analytical EQP 300 spectrometer. The mass spectrometer orifice, located at a distance of \(100\) mm from target center, was electrically...
The synchronized bias configuration, a negative pulsed bias $U_{p} = 50$ V with a duration of $100 \mu$s, i.e., the same pulse duration as the target voltage pulse, is applied with a time delay $\Delta t$ of $60 \mu$s from the onset of the applied target voltage pulse. The selected $\Delta t$ ensures that the metal ion flux at the substrate is maximized, as determined by the plasma characterization demonstrated in Sec. III A. As for a bias scheme for gas-dominated ion irradiation, deposition using continuously applied DC bias at the same level of $U_{f} = 50$ V was performed for comparison. In addition, the impact of various metal ion energies during film growth was also studied by increasing the synchronized bias voltage to $U_{f} = 100$ and $200$ V using the same timing. All depositions above were performed at the same discharge conditions, resulting in a peak current density $J_{\text{peak}} \approx 0.75$ A/cm$^2$ in the Ar atmosphere.

The effect of reducing backscattering of inert working gas atoms at the cathode target was also explored by using Kr instead of Ar. Discharge conditions for the Kr atmosphere was selected to obtain the same average power of 280 W but a lower peak current density $J_{\text{peak}} \approx 0.45$ A/cm$^2$ due to the voltage limitation of the power supply.

A deposition time of 30 min was used for all depositions, and the resulting film thicknesses are listed in Table III. Higher deposition rate (as seen by a higher averaged film thickness) for the Kr process is attributed to the higher sputtering yield of tungsten by Kr$^+$ ions ($S_{Kr}^{Kr+} \approx 1.35$ at 950 eV accelerated across the cathode sheath) compared to Ar$^+$ ions ($S_{Ar}^{Ar+} \approx 0.74$ at 800 eV).

Crystal structure analysis of the deposited samples were carried out by high-resolution x-ray diffraction (XRD) using a PANalytical Empyrean diffractometer, equipped with a PIXcel-3D detector, using Cu-K$_{α}$ radiation ($\lambda = 0.154 059 7$ nm). $θ-2θ$ scans between 35° and 120° were performed with line-focus and an x-ray mirror with a two-bounce Ge monochromator as an incident-side and a parallel plate collimator as a diffracted-side optics. The observed strong α-[110] film texture ($θ = 40.265°$) motivated detailed scans in a narrower range of 39°–41° with a 0.002° step size. Both $θ-2θ$ and grazing incidence (GI) scans, at an incident angle of 1°, were performed. Diffraction peaks from the GI scan were utilized to estimate the grain sizes as determined by applying Scherrer’s equation.

The same XRD instrument but with different optics, point focus, a four-bounce Ge (220) monochromator as an incident-side and a three-bounce Ge (220) monochromator as a diffracted-side, was used to study the macroscopic residual stresses in the deposited films from the curvature of the single-crystal substrate. The curvature was assessed by the change in orientation of a diffracting crystallographic plane at two different location of the sample surface. The Stoney formula for anisotropic single-crystal Si (001) was used to extract residual coating stress from the measured substrate curvature. Here, uniform plane stress in the film was assumed.

XRD pole figure measurements were systematically carried out on α-[110] and α-[200] diffraction peaks in order to determine the main texture component. Point focus and x-ray lens as incident optics and the same diffracted-side optics as for the $θ-2θ$ scans were used. The scans were performed at ϕ-angles (angle between the normal to the sample surface and the normal to the diffracting planes) ranging from 0° to 85° with a 5° step and ϕ-angles (rotational angle around the normal to the sample surface) between 0° and 360° with a 5° step. The integration time was 1 s per point.

### Table I. List of the monitored OES lines with corresponding wavelength $\lambda$, the transition strength $A_{k\lambda}$, and the energy of lower $E_1$ and upper $E_k$ transition levels.

| OES lines | $\lambda$ (nm) | $A_{k\lambda}$ ($\times 10^6$) (s$^{-1}$) | $E_1$ (eV) | $E_k$ (eV) |
|-----------|----------------|---------------------------------|------------|------------|
| Ar I      | 763.51         | 0.25                            | 11.54      | 13.17      |
| Ar II     | 427.75         | 0.80                            | 18.45      | 21.35      |
| W I       | 255.13         | 1.78                            | 0.00       | 4.86       |
| W II      | 276.42         | 0.48                            | 0.00       | 4.48       |

Tungsten films were grown onto Si (001) substrates with a 100 nm-thick thermally grown oxide layer. Prior to the depositions, the substrates were cleaned using successive rinses in ultrasonic baths of acetone followed by isopropanol and finally blown dry with N$_2$. They were then mounted on a substrate stage located at a distance of 100 mm from the target surface, the same as for the mass spectrometer orifice.

To investigate the effect of gas- vs metal-ion acceleration, the depositions were conducted using different substrate bias configurations: floating bias, continuously applied (DC) bias, and synchronized pulsed bias, as summarized in Table III. For grounded during the experiments. Ion energy distribution functions (IEDFs) were scanned from 1 to 50 eV for W$^+$ and W$^{2+}$, and from 1 to 30 eV for Ar$^+$ and Ar$^{2+}$ ions, in 1 eV steps, while sputtering under the conditions stated above. All measurements were carried out with the same global spectrometer settings obtained by calibrating the mass spectrometer to Ar$^+$ ions to allow comparisons between the different ion species. However, it should be noted that no attempts have been made to adjust the measurements for spectrometer performance at different ion energies, such as focal length of the electrostatic lenses and acceptance angles of the sampling orifice. In order to acquire time-resolved data, the detector gate of the mass spectrometer was synchronized with the target-pulse onset, triggering by a transistor–transistor logic pulse sequence generated at the output of the HiPSTER synchronization unit. The detector gate width was set to 10 $\mu$s and the delay time with respect to the onset of the voltage pulse to the cathode was varied from 50 $\mu$s up to 400 $\mu$s in 10 $\mu$s intervals. The total acquisition time per data point was 10 s, implying that data were collected during 100 consecutive pulses for the used pulse frequency of 100 Hz. All time-resolved data presented were corrected for the ion time-of-flight (TOF) within the mass spectrometer, following the procedure of Bohlmark et al. and listed in Table II for the lowest and highest incident kinetic energies.

### Table II. Ion species, mass/charge (m/z) ratios, incident ion-kinetic-energy ranges, corrected TOF values, and energy-averaged TOF values.

| Ion species | m/z  | Kinetic energy range (eV) | TOF (μs) | Average TOF (μs) |
|-------------|------|--------------------------|----------|-----------------|
| 40Ar$^+$    | 40   | 1–100                    | 75–79    | 77.0            |
| 40Ar$^{2+}$ | 20   | 1–100                    | 53–56    | 54.5            |
| 184W$^+$    | 184  | 1–100                    | 162–170  | 166.0           |
| 184W$^{2+}$ | 92   | 1–100                    | 114–120  | 117.0           |
The microstructures of selected W samples were characterized by electron microscopy. The scanning electron microscopy (SEM) analysis was done using a Zeiss LEO 1530 field emission gun instrument. Prior to analysis, cross sections of the films were prepared by first immersing into liquid nitrogen followed by fracturing. The topography of the thin films was analyzed both by plan-view SEM images and by atomic force microscopy (AFM) analyses using a Veeco Dimension 3100 instrument with a Nanoscope IIIa controller, operating in tapping mode under ambient conditions. Root mean square (RMS) roughness was determined from AFM images with an area of $1 \times 1 \mu m^2$ with the image analysis tools of the WSxM ver. 4.0 software.

Selected thin films were chosen for more detailed microstructural investigations by (scanning) transmission electron microscopy (TEM). Prior to analysis, suitable plan-view and cross-sectional specimens were prepared by using a focused ion beam (FIB) instrument (Zeiss 1540). Cross-sectional specimens were prepared by the traditional lift out approach.\(^5\)\(^6\) For plan-view, a sample was prepared by first cleaving to give a wedge shape specimen then using the FIB to thin a $5 \times 7 \mu m$ region below the surface of the film. All analyses were performed using a FEI Tecnai G2 TF 20 UT instrument operated at 200 keV. STEM images were collected with the annular detector spanning the range $80$ to $180$ mrad. All image analysis was performed using the Digital Micrograph software V3 (Gatan, CA), including fast Fourier transmission (FFT) and inverse FFT (FFT\(^{-1}\)) processing. Both FFT and FFT\(^{-1}\) are well established methods applied to the post-processing of HRTEM images.\(^\text{FFT provides an effective diffraction pattern from a HRTEM image, from which selected diffraction spots are used to form a processed image, providing spatial information on specific domains and defects.}\(^\text{FFT provides an effective diffraction pattern from a HRTEM image, from which selected diffraction spots are used to form a processed image, providing spatial information on specific domains and defects.}\)\(^\text{FFT provides an effective diffraction pattern from a HRTEM image, from which selected diffraction spots are used to form a processed image, providing spatial information on specific domains and defects.}\)

Room-temperature electrical resistivities $\rho$ were determined by multiplying the thickness and the sheet resistance of the W film measured by using a four-point probe SRS-4 (Astellatech, Inc.). Thicknesses were determined from step profiles between a coated and a non-coated area by using a Keyence NANOSCALE VN-8000 hybrid microscope. The obtained value was also confirmed from cross-sectional images from the SEM analyses, showing a good agreement between the both measurements. To correlate the amount of incorporation of Ar as an impurity acting as electron scattering centers,\(^\text{relative difference of Ar contents in the films between different bias configurations were additionally analyzed by energy dispersive x-ray spectroscopy (EDS). The EDS measurements were taken in the same system as microstructure analysis operated at an accelerating voltage of 10 kV. The samples were tilted $40^\circ$ from the vertical so that they are normal to the EDS detector. The recorded values are an average of ten measurements taken from randomly selected regions magnified by 1000 (approximate a size of $300 \times 225 \mu m^2$) with errors determined by the standard deviation of the mean.}\)

### III. RESULTS

#### A. Plasma characterization

Prior to the film growth experiments, HiPIMS plasma discharges in the Ar atmosphere were characterized in order to design the substrate bias strategy. Figure 1 shows typical target current $I_c$ and voltage $U_c$ waveforms acquired. The evolution of the discharge current is characterized by an initial peak followed by a slow decrease or a plateau. The onset of the current increase is affected by the applied $U_c$ with steeper current rise for higher voltages, indicating efficient ionization of the Ar gas.\(^\text{After the current peak, a current plateau is observed for $U_c \geq 600$ V. The level of the current plateau increases with $U_c$ up to 30 A for $U_c = 900$ V. This transition at $U_c = 600$ V is likely due to the discharge mode transition from a working gas sputtering regime toward a working gas-sustained self-sputtering or self-sustained self-sputtering mode.}\(^\text{The ion and neutral compositions of the plasma as evaluated with time-resolved OES measurements are presented in Fig. 2. The line intensities are shown for neutrals (Ar I and W I) and for singly ionized ions (Ar II and W II) in a process operated at $U_c = 800$ V with a peak current of $\sim 35$ A ($\sim 0.76$ A/cm$^2$ in peak current density). Ar I increases rapidly at the beginning of the pulse and peaks at $t \approx 4 \mu s$ ($I_p$ peaks at $t \approx 15 \mu s$). When Ar I starts to decay, Ar II, W I, and W II increase and reach a maximum at $t \approx 35 \mu s$. After this, the emission lines converge to plateau levels until the pulse current is terminated. According to Hala \textit{et al.}, the detected emission from neutral Ar at the early stage of the HiPIMS pulse is due to electron impact excitation involving fast secondary electrons accelerated in the developing cathode sheath.\(^\text{The increase of Ar II emission lines is attributed to the ionization of working gas atoms in collision with these energetic electrons. Simultaneously, the increase of W I and W II intensities indicates the injection of metal into the discharge after having been sputtered by working gas ions. The sudden decay of the Ar I is a sign of gas rarefaction of the working gas, which can be particularly pronounced when sputtering heavy elements like tungsten.}\)
To characterize the gas and metal ion fluxes to the substrate plane, in situ time-resolved mass spectroscopy measurements were performed at a distance \(d = 100\) mm away from the target surface. Time-dependent ion flux intensities are presented in Fig. 3 for \(\text{Ar}^+\), \(\text{W}^+\), and \(\text{W}^{2+}\) obtained using the same discharge condition as used for the OES measurements. A small intensity signal from the \(\text{Ar}^{2+}\) flux is also detected (data not shown) with a measured ion intensity \(<3\%\) of the total measured ion intensity. Each data point represents the number of counts integrated during 10\(\mu\)s intervals, and \(t = 0\) corresponds to the onset of the HiPIMS pulse. The ion intensity during the early part of the HiPIMS pulses is dominated by \(\text{Ar}^+\) followed by a rapid increase in the \(\text{W}^+\) intensity and a decrease of \(\text{Ar}^+\) starting at \(t \sim 25\mu\)s. The \(\text{W}^+\) intensity reaches a maximum at \(t \sim 70\mu\)s after which it gradually decays and the \(\text{Ar}^+\) intensity again increases. The time for the \(\text{W}^+\) peak agrees with the \(\text{W}^{\text{II}}\) OES peak taking an estimated time-of-flight (TOF) of \(23\mu\)s into account (10 eV \(\text{W}^+\) traveling the 75 mm from the position where the OES spectrum was obtained). After the pulse has been switched off at \(t = 100\mu\)s, the \(\text{Ar}^+\) flux intensity significantly increases with a delay after pulse off due to a TOF estimated to be \(20\mu\)s for 5 eV \(\text{Ar}^+\) traveling the \(\sim 100\) mm distance from the target region and reaches maximum intensity at \(t \sim 150\mu\)s. The increasing intensity of \(\text{Ar}^+\) during the plasma afterglow phase can be explained by refilling of \(\text{Ar}\) neutrals followed by electron impact ionization by a relatively high density remanent plasma. Poolcharuansin and Bradley investigated Ti/Ar HiPIMS discharges and recorded afterglow electrons with an effective temperature \((T_{\text{eff}})\) of \(\sim 0.2\) eV, which exhibited a slow decay rate of several milliseconds, having a density of \(2 \times 10^9\) cm\(^{-3}\) even at the end of the pulse off-time.\(^{41}\)

To get more insight into the ion flux, detailed time-evolutions of the ion energy distribution functions (IEDFs) were obtained and illustrated in Fig. 4. The first \(\text{W}^+\) ions are detected at \(t = 24–34\mu\)s
[as seen in Fig. 4(a)], and a broad energy distribution with a peak at around 15 eV is seen at \( t = 34\,\mu s \). After that, the IEDFs gradually decrease in energy with time and only consist of thermalized ions accelerated to about 3 eV by the plasma potential after the termination of the HiPIMS pulse. These temporal evolutions of IEDFs are mainly due to the difference in TOF of ions with different energies\(^{44}\) and are consistent with previous mass spectrometry investigations of HiPIMS discharges.\(^{45}\) The origin of the high- and low-energy ions in typical HiPIMS discharges are described elsewhere.\(^{46,47}\)

The time evolution of the \( \text{Ar}^+ \) IEDF, as shown in Fig. 4(b), has a different trend as compared to \( \text{W}^+ \). The first \( \text{Ar}^+ \) ions are detected already at \( t = 13\,\mu s \) and at \( t = 23–33\,\mu s \) their intensity begins to increase, and the energy peak position shifts up to around 2 eV. In the time interval \( t \sim 33–53\,\mu s \), the IEDF decreases in intensity after which it increases again with a broadening of the energy distribution up to 13 eV until \( t \sim 110\,\mu s \), which corresponds to the time directly after the pulse termination. Shortly after the end of the pulse, only the low-energy peak remains as it gradually narrows down to an energy peak centered around 2 eV. The broadening of the energy distribution coincides with the time when the high-energy flux of \( \text{W}^+ \) develops. This can be attributed to the heating of the Ar gas by energy exchange through collisions with energetic sputter-ejected W neutrals, or by Ar reflected at the target, followed by immediate ionization.\(^{24,48,49}\) Although the time these reflected Ar neutrals spend in the dense plasma region would be very short, reflection of Ar onto the target would occur with a high probability due to the large mass difference.\(^{50}\) This latter effect was also found to be significant in HiPIMS discharges using a Ta target, as reported by Rudolph et al.\(^{11,12}\) and should likely be taken into account also here.\(^{51}\)

Overall, the time evolution of the different species investigated by OES and mass spectrometry reveals that depletion of neutral Ar through gas rarefaction occurs at the same time as increasing fluxes of energetic sputter-ejected W neutrals are observed. As a result, metal ions (\( \text{W}^+ + \text{W}^{2+} \)) become dominant between \( t \sim 30–120\,\mu s \), having more than 50% of the recorded total ion intensity. In particular, at \( t \sim 50–60\,\mu s \) when the Ar gas ion intensity reaches a local minimum, the metal ion intensities (\( \text{W}^+ + \text{W}^{2+} \)) represent \( \sim90\% \) of the total recorded ion intensity with the major contribution, \( \sim80\% \) due to \( \text{W}^+ \). Based on these results, the delay time of the synchronized pulsed bias was selected to be \( \Delta t = 60\,\mu s \) (taking into account the TOF for the metal ions to reach the substrate region), as summarized in Table III and described in Sec. II.

### B. Crystal phase and texture analysis

Typical XRD out-of-plane \( \theta-2\theta \) scans (\( \psi = 0^\circ \)) from films grown using the different bias configurations are shown in Fig. 5. For purpose of clarity, the diffractograms are offset vertically and the intensities are displayed on a logarithmic scale to enhance the low intensity part of the diffractogram. Regardless of the bias configurations used, the films exhibit the \( \alpha \)-W (bcc) phase with a predominant \( \alpha\{-110\} \) crystal plane texture, which is commonly reported in the literature for the growth of \( \alpha \)-W films by sputtering.\(^{53}\)

Although the presence of the \( \beta \)-W phase cannot be excluded directly from these data due to the overlap between \( \alpha\{-110\} \) peak (\( 2\theta = 40.265^\circ \)) and \( \beta\{-210\} \) diffraction peak (\( 2\theta = 39.866^\circ \)), any significant amount of the \( \beta \)-W phase could be ruled out from the pole figures and the electron diffraction patterns from TEM images shown later in this section. Besides the dominating \( \alpha\)-W peaks, a weak \( 2\theta \sim 222 \) peak is observed for the films deposited using a continuous bias at \( \Delta t = 50\,\mu s \) and a \( 2\theta \sim 211 \) peak for the film deposited using synchronized bias at \( \Delta t = 200\,\mu s \) as well as for the film deposited using Kr gas.

High-resolution \( \theta-2\theta \) out-of-plane scans of the \( \alpha\{-110\} \) peak are shown in Fig. 6. The Bragg angle for the unstrained reflection is shown as a dotted line in the figure. The XRD scans reveal changes in the \( \alpha\{-110\} \) peak intensity, \( I_{110} \), the full width at half maximum (FWHM), and peak position depending on the choice of bias configuration and working gas. An increase of the \( I_{110} \) is demonstrated from \( 1.3 \times 10^5 \) cps at floating conditions to \( 2.3 \times 10^6 \) cps by applying continuous \( \Delta t = 50\,\mu s \), which is further increased to \( 4.9 \times 10^7 \) cps by synchronizing a pulsed bias with the metal-rich portion of the HiPIMS pulse. The results clearly indicate enhanced crystalline quality for tungsten films grown under synchronized \( \Delta t \) configuration. Moreover, increasing \( \Delta t \) in synchronized bias configuration
resulted in $I_{110} = 7.2 \times 10^3$ cps for $U_s = 100$ V and $I_{110} = 1.7 \times 10^4$ cps for $U_s = 200$ V. The latter intensity is an order of magnitude higher than that obtained with continuous $U_s$. The tungsten film grown in the Kr discharge exhibits a rather low intensity of $I_{110} = 2.0 \times 10^3$ cps.

To get a better understanding of the variations in both the FWHM and shift of the $\alpha$-{110} peak position, the FWHM value $\Gamma_{2\theta}$ and the crystal lattice parameters are plotted in Fig. 7. The unstrained lattice parameter for $\alpha$-W is indicated with a red dotted line as a reference. By changing the bias mode from continuous to synchronized $U_s$ mode, $\Gamma_{2\theta}$ decreases from 0.75° to 0.68° even under the same $U_s = 50$ V and decreases further to $\Gamma_{2\theta} = 0.57°$ by increasing synchronized $U_s$ to 200 V. Moreover, by changing the working gas to Kr, $\Gamma_{2\theta}$ decreases to 0.45°. A similar decreasing trend of the lattice parameter from 0.3202 nm at floating $U_s$ mode to 0.3193 nm by applying synchronized $U_s$ mode was observed. A further decrease to ~0.3176 nm was obtained by increasing the synchronized $U_s$ level and by using Kr as working gas. These results clearly illustrate the reduction of the compressive stress levels achieved upon changing the $U_s$ mode. To confirm the stress state in the films, residual stresses were measured utilizing the substrate curvature of the thermally oxidized Si (001) substrate and calculating the stress using the Stoney formula.32 Obtained results in Fig. 7 clearly demonstrate the relaxation in compressive stress from $\sigma = -1.79 \pm 0.11$ to $\sigma = -1.43 \pm 0.15$ GPa upon changing the $U_s$ mode from continuous to synchronized mode. Increasing the synchronized $U_s$ level contributes to further reduction to $\sigma = -0.71 \pm 0.04$ GPa at $U_s = 200$ V. Moreover, extremely low tensile stress with $\sigma = 0.03 \pm 0.08$ GPa was obtained using the synchronized bias mode and Kr.

To study the film texture in more detail, XRD pole figures of the [110] and [200] planes in $\alpha$-W were obtained. Typical $\alpha$-{110} pole figures for the W films deposited at continuous and synchronized $U_s = 50$ V using Ar and Kr are displayed in Fig. 8. The results clearly show the dramatic changes in film texture as bias mode and
working gas are changed. To display these variations in a comprehensive way using radial intensities, sectional profiles of the pole figure intensities are given in Fig. 9. Negative and positive degrees indicate integrated intensity values obtained from different 180° sectors. The indices given in the top of the figure indicate the out-of-plane direction of the crystal in case a peak appears at that position. The intensity profile for the continuous $U_s = 50$ V configuration reveals peaks at $\psi \sim \pm 35^\circ$ and $\pm 55^\circ$, for the $\alpha$-[110] and [200] diffracting planes, respectively. These angles match the angle of $35.26^\circ$ between $\langle 110 \rangle$ and $\langle 111 \rangle$ and the angle of $54.74^\circ$ between $\langle 200 \rangle$ and $\langle 111 \rangle$ in a cubic structure. This illustrates a $\langle 111 \rangle$ fiber orientation of the film in the growth direction. It has been reported in growth of tungsten films, which is believed to be due to ion channeling. For a bcc lattice, the channeling direction is known as more favorable in $\langle 111 \rangle$. The other peak at the center of the $\alpha$-[110] pole figure and the shoulder at around $\psi \sim \pm 45^\circ$ in the $\alpha$-[200] (angle between $\langle 200 \rangle$ and $\langle 110 \rangle$ in cubic crystals) indicates the presence of a secondary fiber texture component of $\alpha$-[110], which is similar to what has been reported by Girault et al.

By changing to the synchronized bias mode, the $\langle 110 \rangle$-fiber texture becomes gradually more dominant as the bias voltage is increased. This can be concluded from the increasing peak intensity at the center and at $\pm 60^\circ$ ($\psi \sim \pm 60^\circ$ corresponds to the angle between the equivalent directions of $\langle 110 \rangle$) in the $\alpha$-[110] in Fig. 9(a), and at $\psi \sim \pm 45^\circ$ in the $\alpha$-[200] plot with increasing synchronized $U_s$ level up to 200 V [Fig. 9(b)]. Instead, the intensity correlation with

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![Graphs showing pole figures for different conditions](image)

**FIG. 9.** Typical $\alpha$-W $\{110\}$ pole figures of the W films grown with (a) continuous bias $U_s = 50$ V, (b) synchronized bias $U_s = 50$ V using Ar, and (c) synchronized bias $U_s = 50$ V using Kr.
(111)-orientation for the higher synchronized bias voltages of $U_s = 100$ and 200 V becomes less pronounced.

For the Kr sputtered tungsten film, a completely different trend is shown. Both the (110) and (200) pole figures show that the film does not have such a strong fiber texture as the films grown using Ar. A broadening of the intensity from the center to around $\psi \sim \pm 35^\circ$ in the $\alpha$-[110] pole figure are due to grain growth shifting toward the $\langle 211 \rangle$ direction.

The studied pole figures also allow us to investigate the possible misinterpretation of the film texture as being a presence of the $\beta$-W phase in the films. If we instead of $\alpha$-[110] assume $\beta$-[210] in the pole figure, which has an overlapping with $\alpha$-[110] at $2\theta \sim 40^\circ$, radial intensity peaks should be seen at $\psi \sim \pm 37^\circ$ or $\pm 67^\circ$, corresponding to the angle between equivalent directions of (210). These peaks could not be observed, and therefore we conclude that the films contain no detectable amount of $\beta$-W.

C. Microstructure observation

SEM micrographs of fracture cross sections of selected thin films in Fig. 10 show a columnar growth for all of the films deposited in this study. The film grown at $U_s = 50$ V has the narrowest columns for the Ar deposited sample having a 50 ± 15 nm in average width near the film substrate interface increasing to 100 ± 27 nm near the film surface, indicating competitive columnar growth. Films grown at $U_s = 100$ and 200 V clearly have wider columns showing 137 ± 27 and 198 ± 52 nm in average throughout the film thickness, respectively. The films grown using Kr also show a columnar grain structure throughout the film thickness, although it is difficult to estimate the width from the SEM images. However, in the latter part of this section, the columnar width was estimated to be around 50–100 nm from plan-view SEM and the cross-sectional STEM images in Figs. 11 and 12.

To further investigate this change in grain growth between Ar and Kr sputtered films, microstructural characterizations of the surfaces were carried out on the films grown in synchronized bias mode at $U_s = 50$ V using both Ar and Kr as working gas. Figure 11 shows plan-view SEM images for both samples and their corresponding AFM images and associated sectional profiles. Both SEM and AFM show streaked or rippled features on the Ar-grown films with a size of less than 20 nm [Figs. 11(a) and 11(b)]. These nanoridge patterns resemble structures reported by Singh et al., who explained their formation as a result of anisotropic diffusion of sputtered W particles over the $\alpha$-W (100) surface.55 The sizes of the grains are in the range of 100–200 nm, which correlate well with the columnar width observed by SEM (Fig. 10). The Kr sputtered film consists of elongated grains with a faceted surface [Figs. 11(c) and 11(d)] with 10–50 nm width and 100–200 nm length. These facets contribute to the rougher surface observed for Kr sputtered films as compared to the case of Ar. The RMS value, as determined by AFM, is approximately a factor of three higher for the Kr sputtered film.

In-depth observations of the microstructure of the films were carried out using (S)TEM analysis of plan-view samples prepared to visualize the microstructure of the upper part of the films (top 50–70 nm region). Figures 12(a), 12(b), 12(d) and 12(e) show plan-view high angle annular dark-field (HAADF)-STEM micrographs and corresponding selected-area electron diffraction (SAED)
patterns from the films grown under synchronized $U_s = 50$ V using Ar and Kr as the working gas. The SAED pattern in Fig. 12(a) from the film deposited by using Ar contains the intense $\alpha$-110 diffraction ring, together with several diffraction rings from lattice planes (211, 220, 222, and 321), which can be fitted to the expected tungsten structure, in agreement with the pole figure measurement in Fig. 10. In addition, the grain structure observed in Fig. 12(c) resembles the observation from Figs. 11(c) and 11(d), showing elongated grains. Cross-sectional STEM in Fig. 12(f) reveals no evidence for the formation of sub-grains seen for the Ar deposited film in Fig. 12(c). Additionally, EDS analysis were performed on the cross-sectional samples shown in Figs. 12(c) and 12(f) for both Ar and Kr sputtered films. Although compositional quantification and its spatial mapping are difficult, qualitatively the presence of O was clearly confirmed in both cases. Detailed analysis of high-resolution TEM micrographs, shown in Fig. 13, was carried out to investigate the localized concentration of defects. Starting from the FFT of the HRTEM images, masks were applied on selected spots for Ar [Fig. 13(b)] and Kr sputtered films [Fig. 13(g)] to highlight a specific set of atomic planes from each grain. Then, to identify the location of specific defects, an inverse FFT algorithm was performed to reconstruct filtered real space images, which were superimposed on the HRTEM images as shown in Figs. 13(c) and 13(h). These results highlight the positions of specific defects as shown in insets 1 and 2, where different regions display defects such as lattice distortions and dislocations in the masked atomic planes. The HRTEM analysis show that the grain boundaries are fully dense in the case of Ar sputtered films, while underdense structures are shown in the case of Kr. The densification of the grain boundaries leads to the formation of defects in their vicinity, which appear to propagate into the grain, as can be seen in Fig. 13(d) for the Ar sputtered film. The presence of these defects will also result in electron scattering and increase the electrical resistivity of the film, as clearly indicated in Sec. III D, while in the case of Kr sputtered films in Figs. 13(i) and 13(j), defects are observed but with much lower concentration. Overall, a clear evidence of residual defects near the grain boundaries are demonstrated for Ar sputtered films, while the grains for the Kr sputtered film appears to have a microstructure with much lower defect density.

D. Electrical resistivity

The electrical resistivities of the tungsten films deposited under the different bias configurations are presented in Fig. 14. The resistivity decreases from 44.2 to 34.7 $\mu\Omega$ cm by changing the
bias mode from continuous to synchronized, and it further decreases to 18.3 μΩ cm by increasing the synchronized bias voltage from $U_s = 50$ to 200 V. The film grown using Kr exhibits the lowest resistivity, 14.2 μΩ cm. This is obtained without intentional heating of the substrate or post-annealing. Since all films in this investigation have the same crystal phase, α-W, the difference in resistivity between the films must arise from electrons scattering on external surfaces (top surface and film/substrate interface) or on film defects such as grain boundaries and lattice imperfections as can be seen in Figs. 12 and 13.

To analyze the contributions to the difference in resistivity between bias configurations, we focused on the role of Ar impurities in the films, as they are known to increase the resistivity by acting as electron scattering centers. By using a resistivity sensitivity to the incorporation of Ar impurities, $S_{Ar} = 9.1 \, \mu\Omega \, \text{cm/at. %}$, reported by Meyer et al., concentrations of Ar impurities can be inversely calculated using a model proposed by Ligot et al. from the total resistivity obtained above. Details of the calculations are described in the Appendix. To compare the relative trend between the different bias configurations, calculated values are normalized by that from the floating bias configurations, as plotted with open diamond symbols in Fig. 14. Experimental measurements of the Ar content were also performed (EDS) and denoted with filled diamond symbols in the figure. The correlation between the Ar impurity values calculated from the resistivity measurements and measured Ar values are clear except for the highest synchronized bias voltage of 200 V.

**IV. DISCUSSION**

The results presented in Sec. III demonstrate the importance of the choice of substrate bias configuration and working gas (Ar...
or Kr) during W film growth. The selection of ion species for ion bombardment and their energies has a clear effect on defect content and physical properties of the grown films.

The time-resolved plasma characterization reveals that the sputtering process initially generates a gas-dominated ion flux that shifts to metal dominated later in the pulse. After the discharge voltage is switched off, the flux again becomes gas-dominated. The shift from a gas-dominated to a metal-dominated flux is understood to be due to a preferential ionization of sputtered particles as compared to Ar during the HiPIMS pulse due to decreasing electron temperature with increasing discharge current (mainly reduces the ionization efficiency of Ar) and due to working gas rarefaction, which is particularly pronounced when sputtering heavy elements like tungsten. In the present work, this alteration of ion fluxes was used to selectively accelerate the metal ions by changing the bias configurations from continuous to synchronized pulsed bias mode. Based on the mass spectroscopy measurements shown in Fig. 3, 60% of the total ion intensity was W ions at the time period 60–160 μs from the onset of the HiPIMS pulse. By applying the substrate bias during this time period, the contribution of W ions dominates during film growth. On the other hand, Ar ions dominate the accelerated flux in the continuous bias mode, as 68% of the total ion intensity consisted

![Image](image-url)
of Ar ions, as confirmed by a time averaged acquisition at same discharge conditions.

The above observations allow the correlation between the time evolution of plasma characteristics and film growth by first addressing the evolutions of crystal textures. Factors related with texture evolution for polycrystalline W films have been discussed in the literature, addressing the importance of the minimization of total free energy along with other factors, such as an ion channeling effect, surface stress/strain, and surface energy modification due to mixing effects, which could be enhance at nanometric scales. The former, surface energy minimization effect, is generally driven by thermodynamics and is well known to preferentially promote the growth of a ⟨110⟩ texture.

For films grown using continuous bias, the ⟨111⟩ texture components are found as shown in Fig. 9, contrary to the thermodynamically favored ⟨110⟩ texture. By considering the fact that Ar ions dominate the incident flux in the continuous bias scheme, this could originate from the ion channeling effect, which explains the higher survival rate for the open crystallographic direction (the ⟨111⟩ in a bcc lattice) that channels the incident ions into the lattice with less lattice distortion and a lower sputtering yield as a result.

By changing the bias configuration to synchronized mode, where the preferential acceleration of W ions becomes dominant, transformation to a ⟨110⟩ fiber texture is clearly observed, as shown in Fig. 9. In this situation, efficient momentum transfer by self-ion-irradiation can be expected due to the perfect mass match between the collision partners. Through recoil collisional and forward sputtering processes during self-ion-irradiation, displacive knock-on motion at surface atomic migration events will be initiated combining with atomic relaxation, or “recrystallization,” processes. Such processes can be expected to lead to the generation of islands.
with low-energy [110] crystallographic planes to minimize the surface and interface energy during island growth.\textsuperscript{64} Recrystallization during the coalescence of small clusters is also known to lead to the formation of highly textured grains more easily.\textsuperscript{65}

Moreover, by increasing the synchronized bias voltage to $U_s = 100$ and 200 V, the (110) texture becomes stronger and columnar grains become larger, resulting in lattice relaxation with significant decrease of compressive stress as seen in Figs. 6 and 7. In addition to the above kinetically induced displacement, this could also be attributed to temperature-induced structural changes, for instance, due to ion-induced thermal spikes during film growth.\textsuperscript{61} This thermally induced process may result in secondary recrystallization, also called abnormal grain growth, in which the degree of texture is further enhanced with a much larger in-plane grain size.\textsuperscript{66}

The above observation of the film growth events from the texture evolution can be correlated with stress formation and relaxation mechanisms at the different bias configurations. First, the highest compressive stress ($\sigma = -1.79 \pm 0.11$ GPa) was found for the W films grown using continuous bias, as shown in Fig. 7. This value is very close to the value found by Engwall et al. for HiPIMS $\alpha$-W films ($\sigma \sim -2.5$ GPa at a thickness of 500 nm) deposited at comparable experimental conditions (working pressure of 0.93 Pa, $U_s = -646$ V, $U_c = -45$ V).\textsuperscript{76} High compressive stress was also reported for most of the previously reported $\alpha$-W films in the range of 3–7 GPa.\textsuperscript{3,4,16,18,20,21}

The reason for such a high compressive stress is due to the high flux fraction of energetic species reaching the substrate during film growth. This flux is mainly composed of gas atoms reflected back from the target and plasma ions accelerated across the substrate sheath (mainly $W^+$ and $Ar^+$ ions). The impact of these incident energetic particles produces recoil implantation into the film of surface atoms and entrapment of working gas atoms, and consequently building up compressive stress into the film. Through a series of knock-on mechanisms, the subsurface would also be affected inducing the creation of point defects at grain boundaries and/or interstitial sites above a certain energy threshold.\textsuperscript{77}

The contribution of mean energy deposited per incoming particle $E_{\text{dep}}$ (eV) to the stress evolution from a high-energy vapor flux is expressed by Colin et al., as a sum of the average energy of sputtered atoms, that of backscattered gas atoms and the accelerated energy of ions at substrate sheath, $E_i$.\textsuperscript{68} A gradual increase of compressive stress up to $\sigma \sim -2.5$ GPa was demonstrated with increasing $E_{\text{dep}}$ up to $\sim$80 eV/atome in the case of Ta films, due to the increase in the number of defects created with increasing deposited energy.\textsuperscript{68} In this regard, the contribution of the energy induced by the backscattered gas atoms is large in the case of the present study, as we used a heavy-mass target ($m_{Ar} = 40.00$ amu) as compared with the mass of gas atoms $Ar$ ($m_{Ar} = 39.95$ amu).\textsuperscript{69} According to the model reported by Matsui et al.,\textsuperscript{67} an estimate of the maximum backscattering energy $E_b_{Ar}$ of $Ar^+$ ions in 180$^o$ reflections from a $W$ target atoms yields a maximum $Ar$ backscattering energy $E_b_{Ar}$ = 330 eV, assuming a kinetic energy of the incident $Ar^+$ ions of 800 eV. Due to the elastic collisions during transport, this energy can be somewhat lower than the above estimation.\textsuperscript{67} However, it is still high as compared to the contribution of incident ions entering the substrate sheath, as the average kinetic energy is in the range of $E^b_{Ar^+} \approx 3$ eV for $Ar^+$ and $E^b_{W^+} \approx 13$ eV for $W^+$ ions, as estimated from our mass spectrometry measurements. This high-energy vapor flux will contribute to an increase in the mean energy per deposited particle, leading to the production of gas entrapment at the subsurface level.

By changing the bias configuration to synchronized bias, the compressive stress decreased from $\sigma = -1.79 \pm 0.11$ to $-1.43 \pm 0.15$ GPa as shown in Fig. 7. The stress reduction can be explained by the reduction of trapped Ar in the films, as seen from the $\sim$20% reduction in the amount of Ar in the film when changing the bias configuration (Fig. 14). By the use of synchronized bias, incident ions at the substrate during the remainder of the pulse, mainly composed by Ar ions as shown in Fig. 3, have an energy $E_i \approx 10$ eV (assuming the substrate at floating potential). This is below the bulk lattice-atom displacement threshold, lowering the rate of Ar gas entrapment. However, there is still some gas entrapment due to the energetic backscattered Ar neutrals, which is unaffected by changing the bias configurations. This is clearly seen in the sub-domain structure as shown in Figs. 12(b) and 12(c), and in the lattice distortions shown in Fig. 13(d) and 13(e).

Of greater importance when discussing the stress evolution in this study is a significant drop of compressive stress to $\sigma = -0.71 \pm 0.04$ GPa by the increase of synchronized bias voltage up to $U_s = 200$ V (Fig. 7). Based on the above discussion in the evolution of crystal textures, thermally induced processes seem to be contributing to the film growth at this bias configuration, as the relaxation of crystal lattice and coarsening of the grains were observed as shown in Figs. 7 and 10. Shallowly implanted and trapped gas atoms are, in general, known to be unstable and can be annihilated by diffusion toward the nearest underdense region if sufficient energy is provided, e.g., by ion irradiation.\textsuperscript{71} In the present case, the shallowly implanted hyperthermal W ions selected by the synchronized bias efficiently transfer enough energy to trigger diffusion of entrapped $Ar$ atoms toward underdense regions, i.e., the free surface of the growing film.\textsuperscript{72} This leads to the desorption of $Ar$ inclusions from the growing film, as evidenced by the significant reduction of $Ar$ concentration ($\sim$50% reduction compared when using continuous bias) as shown in Fig. 14. Evidence of the thermally activated diffusion by ion-induced processes is also seen from the larger columnar grain widths for films deposited using synchronized bias $U_s = 100$ and 200 V as shown in Fig. 10. If the trapped region of the $Ar$ gas atoms is in the vicinity of the grain boundaries, it is known to diffuse not only toward the free surface but also toward grain boundaries and to enhance grain boundary motion causing grain coarsening during the film growth.\textsuperscript{72} Consequently, even at the concurrent production of gas entrapment during film growth, thermally induced events attributed to the efficient moment transfer by the selective acceleration of the metal ions rich incident flux contribute to the desorption of rare gas atoms, and thus, the total stress of the films decreases with increasing synchronized bias voltage.

An alternative route to decrease film stress is to simply suppress the origin of $Ar$ gas entrapment, i.e., backscattered $Ar$ neutrals, by using heavier sputtering gas as presented in the case of Kr sputtered films. Effects of the selection of sputtering inert gas in W film growth has been thoroughly studied in ion beam sputtering by Hoffman et al.\textsuperscript{73} By the use of Kr gas instead of $Ar$ under the primary ion energy of 600 eV, trapped gas composition
was significantly reduced from 1.97 to 0.06 at. %, resulting in a reduction of residual compressive stress from $-2.7$ to $1.3 \text{ GPa}$. In the present case, by assuming the incident Kr$^+$ energy of 950 eV, the corresponding maximum backscattering energy for Kr$^+$ is $E_{\text{Kr}} = 133 \text{ eV}$. This is 1/3 of the value estimated in Ar process, and it will clearly contribute to reduce the production of rare gas entrapment, leading to a reduced fraction of point defects in the films as we confirmed by the HRTEM and inverse FFT analysis in Figs. 13(f)–13(j). This is, in fact, also shown by the almost unstrained crystal lattice with extremely low tensile stress $\sigma = 0.03 \text{ GPa}$ (Fig. 7) resulting in the lowest resistivity of 14.2 $\mu\Omega \text{cm}$ for Kr sputtered films (Fig. 14). This was achieved without increasing the substrate potential to $U_s = 200 \text{ V}$ as in the case of Ar sputtered films.

One important aspect concerning the Kr sputtered films is the slightly narrower columnar growth with lesser degree of preferred orientation as can be seen in Figs. 8–12. One reason for limited grain coarsening during growth of Kr sputtered films can be explained by the low production rate of defects. Atwater et al. investigated grain growth mechanisms enhanced by ion bombardment during growth of Ge, Si, and Au films. They highlighted the importance of thermal migration of bombardment-generated defects across the boundary by showing the proportional relation between grain boundary motion and the defect concentration at the boundary.

Another possible explanation for limiting grain growth could be due to impurities, in particular oxygen, which still is present at the base pressure used in the present study ($\sim 8.0 \times 10^{-4} \text{ Pa}$). The influence of incorporation of atmospheric contaminants, such as oxygen, on the changes in film structure and grain orientation are summarized as a function of a ratio of oxygen flux to Ar flux during growth of Ge, Si, and Au films.

The ion-composition is initially and finally gas dominated, but there is a window ranging from $t = 30–120 \mu\text{s}$ after the HiPIMS pulse where metal ions are dominating, having more than 50% of the total ion intensity. This is due to a combination effect of efficient ionization of sputtered particles during HiPIMS pulse and a strong working gas rarefaction. By applying a synchronized pulsed substrate bias at the metal dominated portion, films that normally (using a continuous bias) achieve a (111) transform to highly (110) textured films. We also find that by increasing the synchronized negative pulsed substrate voltage from $U_s = 50$ to $200 \text{ V}$, there is a general increase of columnar size, a higher degree of preferred orientation, and a lattice relaxation resulting in a lower film compressive stress. Concurrent reduction of Ar incorporation by the increase of $U_s$ suggested the contribution of the efficient momentum transfer by the selective W ion irradiation to kinetic collision cascades and the consequent thermally induced events, which help anneal out defects and desorb trapped noble gas atoms.

The quality of the films can be further enhanced by the suppression of the high-energetic backscattered Ar gas atoms by shifting to Kr. In this case, a fully relaxed crystal lattice with almost no stress, only $\sigma = 0.03$, was demonstrated. This is all achieved without the need for substrate heating or post-annealing, that are normally needed to achieve comparable film properties.

Finally, it is concluded that the large contribution of W ions dominated fluxes and their selective acceleration will provide efficient momentum transfer, which enhances surface adatom mobilities and consequent annihilation effects even at low deposition temperatures. This will potentially open up more efficient pathways for reducing ion-induced point defects and compressive stress for pure metallic films even for the ultra-thin (few tens of nm-thick)
range for, e.g., interconnect materials for semiconductor metallization like Cu, Co, and Ru.\textsuperscript{77}

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**APPENDIX: INVERSE CALCULATION OF AR IMPURITIES FROM TOTAL ELECTRIC RESISTIVITY**

We are interested to see if we can draw any conclusion on which of the remaining factors that dominate the observed resistivity values. We have the XRD-measurements that, through the peak broadening, give us an estimate of the defect content of the films and film impurities are expected to be dominated by atoms from the residual gas in the vacuum system (mainly water) and from the sputtering gas (Ar or Kr). It is generally observed that reactive impurities, such as O and OH, in the grain boundaries,\textsuperscript{16} while noble gas atoms can be included in the W lattice through energetic implantation.\textsuperscript{26} Mayadas and Shatzkes proposed a model assuming polycrystalline thick films consisting of a columnar grain with an average diameter \(d\).\textsuperscript{16} In their model, the scattering probability of electron waves at the grain boundaries is taken into account by the reflection coefficient \(R\). The intrinsic resistivity \(\rho_{\text{int}}\) can then be described by

\[
\rho_{\text{int}} = \rho_0 \left[ 1 - \frac{3}{2} \alpha + 3\alpha^2 - 3\alpha^2 \ln \left(1 + \frac{1}{\alpha}\right) \right]^{-1}, \quad (A1)
\]

where

\[
\alpha = \frac{\lambda_e}{d} \frac{R}{1 - R}, \quad (A2)
\]

Here, \(\rho_0\) is the bulk resistivity and \(\lambda_e\) is the electron mean free path (19.1 nm for bcc W at 293 K).\textsuperscript{76} Hence, \(\rho_{\text{int}}\) of the W films can be described using the two variables \(\rho_{\text{int}} = \rho_0 F(R, d)\). To estimate the intrinsic resistivity \(\rho_{\text{int}}\) for the present W films under different bias configurations, \(d\) is set to be the Scherer size estimated from GI-XRD scans. To establish an upper level of the effect from the grain boundaries, we assume \(R\) to be 0.65, which is the highest value reported for W films that we can find.\textsuperscript{8}

If we make the bold assumption (\(R\) is constant for these films) that the deviation between the experimental and calculated resistivities are due to lattice defects, we can follow Ligot et al.\textsuperscript{76} that the increase of resistivity due to the incorporation of impurities, \(\rho_{\text{imp}}\), can be approximated to be the sum of effects from different impurities,\textsuperscript{6}

\[
\rho_{\text{imp}} = S_n \times \text{at.\%} (n), \quad (A3)
\]

where \(n\) is an atomic element and \(S_n\) is the sensitivity of resistivity for that element in the W. The dominating lattice impurity in the present W films is believed to be the noble gas. Ligot et al. gave the value of \(S_\text{Ar} = 9.1 \mu\Omega\text{cm/at.\%}\). By assuming total resistivity obtained in the resistivity measurement is a sum of \(\rho_{\text{int}}\) and \(\rho_{\text{imp}}\) atomic concentrations of Ar in the W films can be inversely estimated using Eqs. (A1)–(A3).

**DATA AVAILABILITY**

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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