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High-Power Impulse Magnetron Sputter Deposition of TiB_x Thin Films: Effects of Pressure and Growth Temperature

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Titanium boride, TiB_x , thin films are grown in pure Ar discharges by high-power impulse magnetron sputtering (HiPIMS) from a compound TiB_2 target. Film compositions are determined by time-of-flight elastic recoil detection analysis and Rutherford backscattering spectrometry as a function of deposition temperature ($T_s = 25 - 900$ °C) and Ar pressure ($p_{Ar} = 0.67 - 2.67$ Pa, $5 - 20$ mTorr). For reference, films are also grown by direct current magnetron sputtering (dcMS) under similar conditions. The HiPIMS waveform, average target power $\mathcal{P}_T$, and resulting film compositions are strongly dependent not only on p_{Ar} , but also on T_s . At high pressures the effect of varying T_s on $\mathcal{P}_T$ is minimal, while at lower p_{Ar} the effect of T_s is more pronounced, due to substrate-temperature-induced gas rarefaction. Films grown by HiPIMS at 0.67 Pa are understoichiometric, with $\text{B/Ti} = 1.4 - 1.5$, while at 2.67 Pa, B/Ti decreases from 2.4 to 1.4 as T_s increases from 25 to 900 °C. dcMS-deposited films are overstoichiometric ($\text{B/Ti} \simeq 3$) when grown at low pressures, and near-stoichiometric ($\text{B/Ti} \simeq 1.9 - 2.2$) for higher p_{Ar} .

All experimental results are explained by differences in the ionization potentials of sputtered Ti and B atoms, together with p_{Ar} - and T_s -dependent gas-phase scattering.

Keywords: Titanium diboride, HiPIMS, ionization, gas phase transport, stoichiometry

1. Introduction

Transition-metal diborides in general, [1] and TiB_2 in particular, have attracted considerable attention due to their distinctive set of properties, including high hardness, [1-12] good electrical and thermal conductivity, [12] as well as excellent thermal and chemical stability. [1-4] Thin films of TiB_x have been grown by a variety of techniques; chemical vapor deposition, [13-16] electroplating, [17] cathodic arc deposition from a compound target, [18,19] reactive sputtering in Ar/ B_2H_6 mixtures, [20] pulsed magnetron sputtering, [21] rf sputtering, [22] high-power impulse magnetron sputtering (HiPIMS) in Ar, [23-26] and direct-current magnetron sputtering (dcMS) from a compound TiB_2 target in Ar. [3-11,27-31] The latter remains the most frequently applied deposition method.

A common issue with dcMS-deposited TiB_x layers is that films grown from a TiB_2 target at low Ar pressures ($\lesssim 5$ mTorr, 0.67 Pa) are typically overstoichiometric with B/Ti ratios of 2.4 to 3.5. [4,5,30,31] Since TiB_2 is a line compound, excess B segregates to grain boundaries, forming interesting nanostructures. [3] Neidhardt et al. explained the mechanisms leading to excess B incorporation in magnetron sputter-deposited TiB_x films; due to the mass difference between Ar^+ ions and the TiB_2 target species, B is ejected preferentially along the target normal, while Ti atoms angular ejection is under-cosine, extending toward larger angles compared to an ideal cosine distribution. Increasing the sputtering pressure and/or the target-to-substrate distance reduces the Ti deficiency due to higher gas-phase scattering of lighter B vs. heavier Ti, atoms. [30]

Petrov et al. demonstrated an approach for obtaining stoichiometric TiB₂ films by applying an external magnetic field along the substrate-to-target axis. [31] Sputtered Ti atoms are selectively ionized due to a lower ionization potential and a shorter gas-phase mean free path. The Ti⁺ ions are steered to the growing film via a *tunable* magnetic field from an external Helmholtz coil, thus providing control of the B/Ti ratio.

In HiPIMS, short high-power pulses are applied to the target, rather than a constant discharge power as in dcMS. [32] This results in a significantly higher degree of sputtered-species ionization, and thereby higher plasma densities, as well as strong gas rarefaction in front of the target, leading to the temporal separation of gas-ion and target-ion fluxes, which enables additional control over alloy and compound film composition, as well as film stress control. [33-37] To date, only a few groups have grown TiB_x by HiPIMS from a TiB₂ target in pure Ar discharges. Zhang et al. [23] investigated the effect of applying a negative substrate bias voltage V_s (up to 200 V) to films grown at $T_s = 200\text{-}300\text{ }^\circ\text{C}$, but film compositions were not reported. Nedfors et al. carried out HiPIMS depositions at $p_{Ar} = 3\text{ mTorr}$, $T_s = 500\text{ }^\circ\text{C}$, a constant target current density of $J_T \sim 0.45\text{ A/cm}^2$, and substrate bias voltages V_s of floating and -60 V, to study the effect of pulse frequency (200-1000 Hz) [24], and later the effect of pulse length (20 and 40 μs) and synchronized bias (-60 V applied for different times during each HiPIMS pulse). [25] They reported B/Ti ratios of 2.3-2.5 (but no correlation with growth parameters was provided) for films grown with 20 and 40 μs pulses. [24] Varying the bias timing affected film texture and stress, but had minimal effect on the composition. [25] More recently, Bakhit et al. varied the HiPIMS pulse duration (30-100 μs) during deposition at $p_{Ar} = 3\text{ mTorr}$ (0.5 Pa) and $T_s = 450\text{ }^\circ\text{C}$. [26] The total power was maintained constant, and therefore, as the pulse length was increased from 30 to 100 μs , the peak current density decreased from ~ 0.90 to $\sim 0.25\text{ A/cm}^2$. The resulting B/Ti ratios increased from 1.83 to 2.08. Nearly stoichiometric films were obtained with 50 μs pulse lengths and $J_T \approx 0.45\text{ A/cm}^2$.

Here, we investigate the role of T_s (25 °C to 900 °C) and p_{Ar} (5 to 20 mTorr, 0.67 – 2.67 Pa) on the composition of TiB_x films grown by HiPIMS from a TiB_2 target, and for a direct comparison, with dcMS under similar conditions. Films deposited by dcMS at $p_{Ar} = 5$ mTorr (0.67 Pa), irrespective of T_s , result in overstoichiometric films ($B/Ti \simeq 3$), while films grown at $p_{Ar} = 20$ mTorr (2.67 Pa) are near-stoichiometric TiB_2 . Most HiPIMS films are understoichiometric, with $B/Ti = 1.4$ -1.5; however, HiPIMS films grown at $T_s = 25$ °C and $p_{Ar} = 20$ mTorr (2.67 Pa) are overstoichiometric with $B/Ti = 2.4$.

2. Experimental procedure

TiB_x films are deposited by HiPIMS and dc magnetron sputtering (dcMS) in a high vacuum system with a base pressure $< 7 \times 10^{-8}$ Torr (9×10^{-6} Pa). The target is a 99.5 % pure TiB_2 disc (Kurt J. Lesker Co.), 76 mm in diameter, mounted on the cathode at a distance of 6.5 cm from the substrate table. Pure Ar (99.9999 %) is introduced into the deposition chamber, via mass-flow controllers, to the desired total pressure, monitored by a capacitance manometer. TiB_x films are grown with Ar pressures of 5 to 20 mTorr (0.67 – 2.67 Pa) and T_s ranging from 25 to 900 °C, as measured by a calibrated thermocouple in the substrate holder.

Si(001) wafers are used as substrates for $p_{Ar} \leq 500$ °C; at higher T_s , the substrates are $Al_2O_3(0001)$ wafers in order to avoid titanium silicide formation at $T_s \gtrsim 600$ °C. [38] All substrates are sequentially cleaned ultrasonically in acetone and isopropyl alcohol prior to loading them into a differentially-pumped load-lock chamber for transport to the deposition chamber. A resistive heater is used and substrates are held at the desired temperature value for at least 30 min, allowing T_s to stabilize, prior to film deposition.

All HiPIMS depositions are performed at a pulse frequency and duration of 100 Hz and 50 μ s (0.5% duty cycle), with a peak current $I_{T,peak} = 40$ A, corresponding to a peak current density $J_{T,peak} = 0.9$ A/cm², and an average power $\mathcal{P}_T$ near 100 W (target power varies with p_{Ar} and T_s , as discussed below). A fixed power of 100 W is used for dcMS film growth ($V_T \simeq 410$ V at $T_s = 25$ °C, and $\simeq 340$ V at 500 °C). All depositions are for 60 minutes, which results in film thicknesses ranging from 300 to 500 nm.

Time and energy-integrated intensities of B^{n+} , Ti^{n+} , and Ar^{n+} ($n = 1, 2$) ions incident at the substrate are measured using a Hiden Analytical EQP1000 mass spectrometer, as has been described previously. [39,40] Film compositions are determined by time-of-flight elastic recoil detection analysis (ToF-ERDA) [41,42] and Rutherford backscattering spectrometry (RBS) at the Tandem Laboratory at Uppsala University.[43] ToF-ERDA is also used to obtain concentrations of light contaminant species, and RBS provides atomic-area densities. ToF-ERDA is carried out with a 36 MeV $^{127}I^{8+}$ beam incident at 67.5° to the sample normal and detected at a recoil angle of 45°. RBS analysis are performed with a 2 MeV $^4He^+$ beam incident at 5°, with a scattering angle of 170°. Additional small tilts are used to minimize channeling effects.

3. Results and discussion

3.1 Plasma discharge characteristics

Figure 1 shows typical target current density $J_T(t)$ and voltage $V_T(t)$ waveforms, as a function of p_{Ar} and T_s , during 50 μ s HiPIMS pulses. Although the peak current density is the same for all deposition conditions, the plasma ignition time, and current rise time, vary with pressure and temperature. Increasing p_{Ar} results in faster plasma response, due to the higher density of ionizable Ar atoms. In contrast, increasing T_s results in slower plasma ignition and current rise

time due to a decrease in gas density. The effect of substrate heating on gas rarefaction, and hence on HiPIMS pulse waveforms, sputtered-atom ionization, and film composition has not been reported previously.

The target voltage at the start of the pulse is ~ 800 V and, due to the limited capacitance bank in the pulsed power supply, decreases to ~ 550 V at the end of the pulse. The average power $\mathcal{P}_T$, obtained by integrating the product $V_T(t) \cdot J_T(t)$ over several HiPIMS cycles, is plotted in Figure 2 as a function of T_s and p_{Ar} . At higher pressures, the effect on $\mathcal{P}_T$ of varying T_s is minimal; $\mathcal{P}_T$ decreases from 124 W at 25 °C to 122 W at 900 °C with $p_{Ar} = 20$ mTorr (2.67 Pa). However, at $p_{Ar} = 5$ mTorr (0.67 Pa), the effect of T_s is pronounced; $\mathcal{P}_T$ decreases continuously from 112 W at 25 °C to 84 W at 900 °C, due to temperature-induced gas rarefaction.

3.2 Ions incident at the substrate

Figure 3 shows the intensities of time- and energy-integrated Ti^+ and B^+ ion fluxes arriving at the substrate during a HiPIMS pulse, as measured by a mass spectrometer at the substrate position. For all p_{Ar} values, the Ti^+ flux intensity I_{Ti^+} is larger than the B^+ intensity I_{B^+} , due to the lower first ionization potential of Ti compared to B (6.8 vs. 8.3 eV [44]) and the higher ionization cross-section. [45] Both I_{Ti^+} and I_{B^+} continuously decrease with increasing p_{Ar} as a result of increased gas scattering. The ratio I_{Ti^+}/I_{B^+} increases from 2.1 to 3.1, as p_{Ar} is increased from 3 to 20 mTorr (0.5 - 2.67 Pa), with $T_s = 25$ °C. Ratios of single- to double-ionized species are $Ti^+/Ti^{2+} \simeq B^+/B^{2+} \simeq 9$ at $p_{Ar} = 3$ mTorr (0.5 Pa), and increase to ≥ 20 as p_{Ar} is increased to 20 mTorr (2.67 Pa). The Ar^+/Ti^+ ratio decreases from 4.7 to 2.1 over the same pressure range.

In order to estimate the effect of T_s and p_{Ar} on gas-phase transport of sputtered flux, we first estimate the ejection energies, E_{Ti} and E_B , of sputtered atoms using TRIM simulations [46] based on the potential of Ar^+ ions incident at the target. In the case of HiPIMS, we also consider sputtering by incident Ti^+ ions during the latter period of each pulse, when $V_T \simeq 550$ V. For the heat of vaporization, which is unknown for TiB_2 , we used a range of values from those of bulk Ti (4.4 eV) and B (5.3 eV) to 8.2 eV, which is typical for refractory materials. [47] The average ejection energy and uncertainty are summarized in Table 1.

We use the sputtered-atom ejection energies E_{Ti} and E_B from Table 1, and the mean-free path $\lambda(T_s, p_{Ar})$ of sputtered species during gas-phase transport, in the “velocity persistence” model of Westwood [48] to estimate the average sputtered-atom distance travelled, L , along the ejection direction before becoming thermalized. λ can be expressed as a function of temperature T and pressure p_{Ar} , via the equation, [48,49]

$$\lambda = \frac{kT_s}{p_{Ar}} \frac{1}{\pi(r_{Ar} + r_{B,Ti})^2} \frac{1}{\sqrt{1 + \frac{m_{B,Ti}}{m_{Ar}}}} . \quad (1)$$

k is Boltzmann’s constant; m is the atomic mass ($m_B = 10.81$, $m_{Ti} = 47.88$, and $m_{Ar} = 39.95$ amu), [44] and r is the atomic radius ($r_B = 0.87$ Å, $r_{Ti} = 1.76$ Å, and $r_{Ar} = 0.71$ Å) of collision partners. [30,44] For simplicity, we assume that the pressure is uniform and the gas temperature is equal to the substrate temperature throughout the entire volume between the target and substrate. In reality, of course, both the pressure and temperature in sputtering discharges vary spatially, and in the case of HiPIMS, also temporally. Hoffman [50] and Rossnagel [51] reported that the gas density in front of the target during dcMS decreases significantly with increasing target current as a result of gas heating, leading to rarefaction, due to momentum transfer from energetic sputtered atoms. During HiPIMS, the effect of gas

rarefaction is much more pronounced. [32-37,52-54] Thus, equation (1) overestimates the gas density near the target. We compare L to the target-to-substrate distance D of 6.5 cm, and the ratio L/D is plotted in Fig. 4, as a function of p_{Ar} and T_s .

The results in Fig. 4 indicate that at $p_{Ar} = 20$ mTorr (2.67 Pa), sputtered Ti atoms are, on average, thermalized prior to reaching the substrate, while at 5 mTorr, $L/D \simeq 1$ at $T_s = 25$ °C, but increases as T_s is increased to 900 °C, due to lower gas densities and hence longer mean-free-paths. The L/D curve for B atoms sputtered at 20 mTorr is slightly below that of Ti atoms at 5 mTorr (0.67 Pa), but both are above $L/D = 1$ for all temperatures. The results also show that L/D is 4-7% higher for HiPIMS compared to dcMS, due to the higher average ejection energy of sputtered atoms. Moreover, L/D during HiPIMS will be even larger due to enhanced rarefaction. Thus, the HiPIMS sputtered flux is less likely than that of dcMS to be thermalized before reaching the substrate.

3.3 Film composition

Figure 5 is a plot of TiB_x film composition B/Ti determined by ToF-ERDA for films grown by HiPIMS and dcMS at 5 and 20 mTorr (0.67 and 2.67 Pa) as a function of T_s . With dcMS, B/Ti decreases from ~ 2.9 to 2 as p_{Ar} is increased from 5 to 20 mTorr (0.67 - 2.67 Pa), at both $T_s = 25$ and 500 °C. This is consistent with previous reports. [30-31] However, HiPIMS films grown at 5 mTorr (0.67 Pa) are understoichiometric, with $B/Ti \simeq 1.4$, irrespective of T_s . At 20 mTorr (2.67 Pa), B/Ti decreases from ~ 2.3 at $T_s = 25$ °C, to 1.6 at 500 °C, and 1.4 at 900 °C.

All TiB_x films have $\lesssim 1$ at % of oxygen, except for HiPIMS films grown at 20 mTorr (2.67 Pa) with $T_s = 25$ °C ($B/Ti = 2.3$) which have 4.1 at% oxygen, and dcMS films grown at 20

mTorr (2.67 Pa) with $T_s = 25$ °C (18.4 at. % O, B/Ti = 1.9) and $T_s = 500$ °C (12.8 at. % O, B/Ti = 2.2). The high bulk oxygen concentrations in the latter three cases indicate that the films are underdense as a result of low average energy of the deposition flux and low adatom mobility. All observed trends in B/Ti and oxygen concentration can be qualitatively explained by differences in the degree of ionization and gas-phase scattering, as discussed below.

Figure 6 shows the atomic deposition fluxes F_{Ti} and F_B , obtained from the combination of RBS and ToF-ERDA analyses, as function of T_s for both HiPIMS and dcMS films grown at $p_{Ar} = 5$ and 20 mTorr (0.67 and 2.67 Pa). With dcMS (Fig 6a), F_{Ti} does not change significantly with either p_{Ar} (data points overlap) or T_s . This is consistent with the results in Fig 4, which show that the dcMS Ti flux is essentially thermalized. F_B has a relatively strong dependence on pressure, and also a slight dependence on temperature. F_B is the highest at $p_{Ar} = 5$ mTorr due to preferential ejection along the surface target normal [30] and minimal gas scattering, resulting in high B/Ti ratios. At $p_{Ar} = 20$ mTorr (2.67 Pa), however, gas scattering results in lower B incorporation, which increases with increasing T_s as the gas density decreases. Thus, at $T_s = 500$ °C, sputtered ejected B atoms retain more of their initial directionality, resulting in the B incorporation increasing by ~25%.

F_{Ti} and F_B during HiPIMS film growth are shown in Figure 6b as a function of p_{Ar} and T_s . The total fluxes, $F_{Ti} + F_B$, are lower than for dcMS, which is a common feature of HiPIMS compared to dcMS performed under similar average target power and deposition conditions. [32,54] However, while F_{Ti} is moderately lower for HiPIMS compared to dcMS, the decrease in F_B is more significant, resulting in lower B/Ti ratios with HiPIMS. This can be explained

by the higher degree of ionization in the HiPIMS discharge; Ti is ionized at a higher rate than B, because of having a lower ionization potential [44] and a higher ionization cross section. [45] The metal-ion-rich plasma is steered to the substrate by stray magnetic field lines from the type-II unbalanced magnetron; thus enhancing the Ti deposition flux relative to that of B. This effect is also present during dcMS, but is significantly more pronounced for HiPIMS due to the higher degree of ionization.

The Ti and B atomic deposition fluxes for HiPIMS at $p_{Ar} = 5$ mTorr (0.67 Pa) are relatively insensitive to the substrate temperature, similar to the case for dcMS, since the sputtered species essentially undergo relatively little gas scattering (see Fig 4). At higher pressures, $p_{Ar} = 20$ mTorr (2.67 Pa), Ti and B atomic fluxes, especially F_{Ti} , increase significantly with increasing T_s , due to the corresponding decrease in gas density. Thus, increasing the deposition temperature has the same general effect as decreasing the pressure; both result in longer sputtered-atom mean free paths and films with higher film B/Ti ratios. Similarly, decreasing the target-substrate distance D would have the same effect as decreasing p_{Ar} and increasing T_s .

4. Summary and conclusions

In summary, we have grown TiB_x films by HiPIMS and dcMS sputtering as a function of Ar pressure ($p_{Ar} = 5$ and 20 mTorr, 0.67 and 2.67 Pa) and substrate temperature ($T_s = 25 - 900$ °C), and demonstrated that the HiPIMS waveform, average target power $\mathcal{P}_T$, and the composition of HiPIMS TiB_x films, are dependent not only on p_{Ar} , but also on T_s . At $p_{Ar} = 20$ mTorr (2.67 Pa) the effect of varying T_s on HiPIMS target power is minimal, while at lower pressures the effect of T_s is pronounced due to temperature-induced gas rarefaction. B/Ti for

HiPIMS increases with increasing T_s , especially at higher Ar pressures, due to temperature-induced gas density reduction. Films grown by HiPIMS are understoichiometric, with B/Ti = 1.4-1.5, with the exception of films grown at 25 °C and 20 mTorr (2.67 Pa), which are overstoichiometric with B/Ti = 2.4. Films deposited by dcMS at 5 mTorr (0.67 Pa), irrespective of T_s , yield overstoichiometric films (B/Ti $\simeq$ 3), while use of p_{Ar} = 20 mTorr (2.67 Pa) results in layers in which B/Ti was tunable from under- to overstoichiometric by increasing T_s . All experimental results are explained as a function of sputtered-atom ionization probabilities, together with p_{Ar} - and T_s -dependent gas-phase scattering.

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Figure captions:

Figure 1: (a) TiB_2 target current density $J_T(t)$ and (b) voltage $V_T(t)$ waveforms recorded during HiPIMS sputtering of TiB_2 in Ar, for selected conditions of Ar pressure p_{Ar} and deposition temperature T_s . The HiPIMS pulse length and frequency are 50 μs and 100 Hz.

Figure 2: Average TiB_2 target power $\mathcal{P}_T$ per HiPIMS cycle vs. substrate temperature T_s for Ar discharge pressures between 3 and 20 mTorr (0.5 - 2.67 Pa). The HiPIMS pulse length and frequency are 50 μs and 100 Hz.

Figure 3: Time- and energy-integrated Ar^{n+} , Ti^{n+} , and B^{n+} ($n=1,2$) ion intensities during HiPIMS sputtering of TiB_2 vs. Ar pressure p_{Ar} . The intensities are measured by a mass spectrometer at the substrate position, 6.5 cm from the target. The HiPIMS pulse length and frequency are 50 μs and 100 Hz.

Figure 4: Ratios of the thermalization distance L of sputtered atoms ejected from a TiB_2 target in pure Ar at $p_{\text{Ar}} = 5$ and 20 mTorr (0.67 and 2.67 Pa) to the target substrate separation D (6.5 cm), plotted as a function of T_s for HiPIMS (solid lines) and dcMS (dashed lines) sputtering conditions. $L/D = 1$ is indicated, for reference, by the dot-dashed line. Error bars are shown to the left for each line.

Figure 5: B/Ti ratios, as measured by ERDA, as a function of substrate temperature T_s , for TiB_x films grown by HiPIMS and dcMS at $p_{\text{Ar}} = 5$ and 20 mTorr (0.67 and 2.67 Pa). Stoichiometric TiB_2 is indicated by the dashed line.

Figure 6: B and Ti atomic deposition fluxes F_{Ti} and F_{B} [atoms $\text{cm}^{-2} \text{s}^{-1}$], determined by a combination of ToF-ERDA and RBS analyses, plotted as a function of film growth temperature T_s for TiB_x films deposited by (a) dcMS and (b) HiPIMS sputtering from a TiB_2 target in pure Ar with $p_{\text{Ar}} = 5$ and 20 mTorr (0.67 and 2.67 Pa).

Tables:

Table 1: Sputtered-atom ejection energies E_{Ti} and E_{B} , based upon TRIM simulations during HiPIMS and dcMS sputtering of TiB_2 at Ar pressures of 5 and 20 mTorr (0.67 and 2.67 Pa) using experimentally determined ion energies eV_T . For HiPIMS, sputtering by Ti^+ ions during the latter portion of each pulse is also included.

Technique	dcMS	dcMS	HiPIMS	HiPIMS
p_{Ar} [mTorr]	5	20	5/20	5/20
Ion	Ar^+	Ar^+	Ar^+	Ti^+
V_T [V]	410	340	800	550
E_{Ti} [eV]	25.2 ± 6.0	24.7 ± 5.0	33.8 ± 8.4	16.0 ± 3.2
E_{B} [eV]	13.9 ± 1.6	13.3 ± 1.2	17.9 ± 2.3	13.4 ± 1.5

Tables:

Table 1: Sputtered-atom ejection energies E_{Ti} and E_B , based upon TRIM simulations during HiPIMS and dcMS sputtering of TiB_2 at Ar pressures of 5 and 20 mTorr (0.67 and 2.67 Pa) using experimentally determined ion energies eV_T . For HiPIMS, sputtering by Ti^+ ions during the latter portion of each pulse is also included.

Technique	dcMS	dcMS	HiPIMS	HiPIMS
p_{Ar} [mTorr]	5	20	5/20	5/20
Ion	Ar^+	Ar^+	Ar^+	Ti^+
V_T [V]	410	340	800	550
E_{Ti} [eV]	25.2 ± 6.0	24.7 ± 5.0	33.8 ± 8.4	16.0 ± 3.2
E_B [eV]	13.9 ± 1.6	13.3 ± 1.2	17.9 ± 2.3	13.4 ± 1.5