Atmospheric Pressure Chemical Vapour Deposition of Thermochromic Tungsten Doped Vanadium Dioxide Thin Films For Use In Architectural Glazing.

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ABSTRACT
Atmospheric pressure chemical vapour deposition of VCl₄, WCl₆ and water at 550 °C lead to the production of high quality tungsten doped vanadium dioxide thin films. Careful control of the gas phase precursors allowed for tungsten doping up to 8 atom%. The transition temperature of the thermochromic switch was tunable in the range 55 °C to -23 °C. The films were analysed using X-ray diffraction, scanning electron microscopy, Raman spectroscopy and X-ray photoelectron spectroscopy. Their optical properties were examined using variable-temperature transmission and reflectance spectroscopy. It was found that incorporation of tungsten into the films led to an improvement in the colour from yellow/brown to green/blue depending on the level of tungsten incorporation. The films were optimized for optical transmission, thermochromic switching temperature,
magnitude of the switching behaviour and colour to produce films that are suitable for use as an energy saving environmental glass product.

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INTRODUCTION

Reducing the energy demands of residential and office buildings by controlling the amount of solar energy entering a building is one step that can be taken in the fight against global warming. One possible way to achieve this is by using a thin film of a thermochromic material on an exterior window [1].

During hot weather a ‘smart’ window would pass all or part of the visible radiation incident on the window and reflect the majority the Sun’s near-infrared radiation; thus the need for the use of air conditioning is diminished. During cooler weather the same level of visible radiation would pass through the window whilst allowing some of the Sun’s near-infrared radiation, limiting the need for internal heating. Such intelligent coatings could be used in a myriad of applications including windscreens of automobiles, sunscreens and greenhouses. The development of such coatings could lead to large savings in energy costs (e.g. power to air conditioning units), improved building environments, and environmental benefits (e.g. reduced CO₂ emissions).

Vanadium dioxide is a thermochromic material that is known to exist in four polymorphic forms; monoclinic VO₂(M) and rutile VO₂(R) and two metastable forms VO₂(A) and VO₂(B) [2]. The monoclinic VO₂(M) converts to rutile VO₂(R) at 68 °C [3]. This is a fully reversible metal to semiconductor phase transition (MST) and is associated with large changes in electrical conductivity and optical properties in the near-IR region [4]. Above 68 °C, VO₂ behaves as a semi-metal and is reflecting to a wide range of solar wavelengths whilst below the MST it behaves as a semiconductor, and reflects significantly less in the near infrared.
Thermochromic properties and thermochromic materials for window glazing applications have been investigated previously [5,6]. By the late 1980's thin-film thermochromic properties had been demonstrated by a number of groups employing physical vapour deposition (PVD) [7] or sol-gel based deposition techniques [1,8-11]. These technology advances were not transferable into commercially relevant products because of inappropriate transition temperatures, low visible light transmission, unattractive visible colours and limited film durability.

Chemical vapour deposition (CVD) is an excellent method for applying thin films to glass substrates during commercial glass manufacture. Atmospheric Pressure CVD (APCVD) has been previously used to deposit VO$_2$ thin films on glass substrates. The process has the advantage of being easily integrated into float-glass production lines and has fast deposition rates. Vanadium alkoxides [12], [V(acac)$_3$] [13], VO(acac)$_2$ [14,15] and various oxovanadium reagents [16] have been used as deposition precursors. Vanadium(IV) chloride and an oxygen source such as methanol or ethanol has been used to prepare V$_2$O$_5$ which was subsequently post-reduced to VO$_2$ by heating in a reducing atmosphere [17], however the films were significantly contaminated with carbon[17]. Aerosol Assisted Chemical Vapour Deposition has also been used to deposit a range of vanadium oxides from V$_2$O$_3$ to V$_2$O$_5$[18].

For thin-films of VO$_2$ to find practical use as smart window coatings, the MST needs to be reduced from 68 °C to a more ambient temperature that will depend on the climate the window is to be used in. Doping metal ions into the VO$_2$ lattice has been shown to increase or decrease the MST temperature ($T_c$) depending on factors such as size [19] and charge [20] of the dopant ion and subsequent changes in electron carrier density [21]. For films produced using PVD, thickness less than 30 nm has also been shown to influence the
thermochromic transition temperature of VO$_2$, this has been explained in terms of a strain effect [16].

Tungsten has been shown to be the most effective dopant ion in reducing the MST of VO$_2$, it can optimally lower the $T_c$ to about 25 °C at 2 atom% loading. Tungsten-doped VO$_2$ films have been previously prepared by sol-gel [1,22], physical vapour deposition methods [7,23] and CVD; both atmospheric pressure [14,24-27] and aerosol-assisted [28].

This paper reports a systematic investigation about the deposition of W-doped VO$_2$ with Atmospheric Pressure CVD; the effect of tungsten on the value of $T_c$ was studied over a range of concentrations wider than ever previously reported. The effect of high tungsten content on the optical properties of the films was also considered, particularly regarding the optical transmission in the visible, the colour and the smart material functional properties (i.e. change in reflection and transmittance with temperature).
EXPERIMENTAL DETAILS

Film preparation

Nitrogen (99.999%, BOC, UK) was used as the system gas in all CVD reactions. The substrates were float glass with a 50 nm-thick SiO$_2$ barrier layer to stop diffusion of ions from the glass into the film (Pilkington Glass, UK). The glass substrates had dimensions 15 cm x 4.5 cm x 0.3 cm and were cleaned prior to use by wiping with a water-soaked tissue, then a propan-2-ol soaked tissue and finally rinsed with propan-2-ol. The substrates were allowed to dry in air prior to mounting in the CVD chamber.

All CVD studies were performed on custom built apparatus using a previously described procedure [24, 25]. VCl$_4$ (99%, Aldrich, UK) and WCl$_6$ (99.9%, Strem, UK) were placed into separate bubblers. Distilled water was injected into the plain line gas-flow using a variable rate syringe driver and either a 1000 µL ‘tuberculin’ syringe or a Hamilton 250 µL gas tight syringe – all of the water was effectively flash evaporated as the plain line was heated to 150 °C. The VCl$_4$ bubbler was set to 50 °C using a flow rate of 0.4 L/min N$_2$, the N$_2$ plain flow was 10 L/min, the mixing chamber temperature 150 °C and the reactor temperature of 550 °C. To alter the VCl$_4$:H$_2$O ratio the speed of the syringe driver injecting the H$_2$O from a 250 µL syringe was varied. The temperature of the tungsten bubbler was varied to change the amount of tungsten in the resultant film. The time of each deposition experiment was varied in order to change the thickness of the resultant film. All films were produced at least in triplicate to check and ensure high levels of reproducibility.

Film analysis and characterization

Analysis of the deposited films consisted of UV/vis absorption, adhesion tests (scratch and abrasion resistance, Scotch tape test), vis/IR reflectance–transmittance, micro-Raman spectroscopy, scanning electron microscopy and wavelength dispersive analysis of X-rays
(SEM/WDX), X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS). The samples were not cleaned prior to analysis. UV/vis absorption measurements were obtained on a Thermospectronic Helios spectrometer between 300-1100 nm. Reflectance–transmittance measurements were performed on a Perkin Elmer Lambda 950 spectrophotometer between 300-2500 nm; transmission measurements were calibrated in air, whilst reflectance measurements were calibrated to a Spectralon standard. The size of the MST and Tc were measured using a Perkin-Elmer 457 grating spectrometer set to 4000 cm\(^{-1}\) and calibrated against the spectrometer transmission in air at 4000 cm\(^{-1}\). An aluminium temperature cell controlled by RS cartridge heaters, Eurotherm temperature controllers and type-K thermocouples was used to control the sample temperature. Measurements below room temperature were made by cooling the thin films sample using solid CO\(_2\) prior to mounting in the temperature cell. Raman spectroscopy was performed on a Renishaw inVia spectrometer using a 514.5 nm 6 mW laser at 50x magnification; sample temperature was controlled by a Linkam THMS600 variable temperature cell with a liquid nitrogen pump. SEM images were obtained on a Jeol JSM-6301F scanning electron microscope at 15 kV accelerating voltage. Samples were prepared by deeply scoring the film side of the substrate to cause shelling of the film and hence a distinct edge between the film and substrate. Wavelength dispersive analysis of X-rays was performed on a Philips XL30 ESEM instrument using Inca analytical software (Oxford Instruments) with an accelerating voltage of 5 kV. X-ray analysis of the films was determined on a Bruker D8 GADDS diffractometer using Cu K\(_{\alpha}\) radiation at 1.54 Å collimated with either a 15 cm long 0.05mm collimator (1-2 mm\(^2\) illumination area) or 7 cm long 0.1 mm collimator (3-5 mm\(^2\) illumination area) with a 5° incident angle. Diffraction patterns at different temperatures were obtained by acquiring discrete data at various temperatures. The temperature was controlled using the aluminium sample holder described above. X-ray photoelectron spectrometry was performed on a VG ESCALAB 2201 XL instrument using
monochromatic Al K$_\alpha$ X-rays with pass energy of 50 eV. Samples were not cleaned prior to use and a flood gun was used to control charging and the binding energies were referenced to an adventitious C 1s peak at 284.8 eV. Depth profile measurements were obtained using argon beam sputtering (etch voltage 5 kV). XPS data was analysed using CasaXPS software version 2.0.11. Samples were subjected to scratch and abrasion tests with a piece of tissue, a brass stylus and a steel stylus. Samples were considered to pass the test if they remained unmarked to the naked eye. Additionally the Scotch tape test was performed; in this test a piece of Scotch tape is placed on the film and removed. The sample fails the test if any of it delaminates and remains on the Scotch tape.

RESULTS

The APCVD reaction of vanadium (IV) chloride, tungsten(VI) chloride and water afforded thin films of un-doped or tungsten doped vanadium dioxide on glass substrates depending on the exact conditions used. The films were a transparent yellow/brown colour in appearance, unless they had more than 2.5 atom% tungsten doping in which case they appeared more blue (but just as transparent) in colour. The films were adherent to the glass substrate and could not be removed by abrasion with a paper towel or the application of Scotch tape. They could however be marked with a brass or steel stylus.

Experimental conditions that reliably produced glassy and adherent films of VO$_2$ were determined. Un-doped VO$_2$ thin films were deposited using a plain flow of 10 L/min N$_2$, with the VCl$_4$ bubbler temperature set to 50 °C and a bubbler flow rate of 0.4 L/min, with a VCl$_4$:H$_2$O ratio of 1:3. The change in optical and functional properties with film thickness were examined to identify the range of film thickness appropriate to give optical transparencies in an acceptable range. Once deposited, the films were analyzed for optical
and functional properties by measuring the room-temperature and high-temperature transmission and reflectance spectra between 300 and 2500 nm. A variety of film thickness (film thickness was determined by cross sectional SEM) were examined to elucidate the most suitable thickness for use in architectural glazing. Figure 1 shows spectra for undoped films with varying thickness.

The 30 nm-thick films had a peak transmission of 77% at 570 nm (Figure 1), as compared to 86% (570 nm) for plain glass, the 80 nm-thick films had a transmission of 60% (570 nm) (Figure 1) and the 150 nm-thick films 15% at 570 nm (Figure 1). As seen previously [14] transmission in the visible decreases with increasing film thickness. The functional properties are also related to thickness. The thinnest film investigated, 30 nm (Figure 1A), had virtually no change in properties when going through the MST. Increasing the film thickness to 80 nm (Figure 1) lead to a 35 % change in transmission at 2500 nm. Increasing the film thickness further to 150 nm (Figure 1) saw a similar change of 35 % at 2500 nm.

The next stage was to investigate tungsten doped films. W-doped VO$_2$ thin films with a thickness of 80 nm were deposited using a plain flow of 10 L/min N$_2$, with the VCl$_4$ bubbler temperature set to 50 °C and a bubbler flow rate of 0.4 L/min, with a VCl$_4$:H$_2$O ratio of 1:3 and with a run time of 60 seconds. The N$_2$ flow rate through the WCl$_6$ bubbler was set to 2 L/min and the temperature of the bubbler varied between 100 °C and 195 °C to change the amount of tungsten in the gas phase.

Scanning electron microscopy (Figure 2) revealed that the films were composed of an agglomeration of irregular particles.
XRD (Figure 3) revealed that the only crystalline phase present was that of monoclinic vanadium dioxide. This was the case for all samples irrespective of the level of tungsten doping.

XPS of the samples revealed that a variety of vanadium oxidation states were present on the surface of the films (Fig 4A) [29]. The species responsible for this are considered to be VO$_2$ and V$_2$O$_5$. Surface oxidation is common with vanadium oxides and has been seen previously [24-27,30]. Upon etching (Figure 4B) the higher oxidation state material (V$_2$O$_5$) diminishes and VO$_2$ is the dominant phase, however quantification of the environments is unreliable after etching. Surface tungsten species were also examined for samples where tungsten was doped at a variety of levels (Figure 4C and 4D) and showed the expected decrease in tungsten content for the films deposited with lower tungsten ratios.

The amount of tungsten in the resultant films was characterized using WDX over a minimum of 10 spots on the film surface (Table 1.). The MST was determined by measuring the $T_c$ temperature using transmission data at 4000 cm$^{-1}$ for those films with $T_c$ above room temperature or with variable temperature Raman spectroscopy to determine those at or below room temperature (Figure 5.).

The MST is easy to characterize using Raman spectroscopy. The low temperature phase has a number of clear bands in its Raman spectrum. The high temperature phase has no discernible bands (has become metallic in nature). In the example shown in Figure 5 the $T_c$ occurs between 4 and 7 °C, i.e. it is 5.5 ± 1.5 °C.
Transition temperature values are presented in Table 1 along with atomic percentages of tungsten doping. The table shows that up to 8.2 atom% tungsten doping could be achieved and that any transition temperature between 55 and -28 °C could be produced. This data indicates a pseudo linear decrease in transition temperature of 22 °C per atom% tungsten doping up until 3.5 atom%; above this doping level, each additional tungsten atom% causes a reduction in transition temperature of 2 °C.

As an example, for a typical film doped with ~ 1.75 % W the optical transmission changed by ~ 40% at 2500 nm between the hot (40 °C) and cold (5 °C) measurements (Figure 6). In this instance the full thermochromic transition is not observed until below room temperature (19 °C). The films also had a transmission of > 60% at 570 nm and as such would be suitable for use in architectural glass.

Another effect of the addition of tungsten to the films was a change in the visible colour of transmission, this can be seen in Table 2, where the LAB colour coordinates for undoped and W-doped thin films are reported. A change of about 100 nm for the dominant wavelength in transmission was observed for W-doped VO₂ samples; this corresponds to a change in colour from yellow/brown to a more aesthetically pleasing silver/blue. The value of the blue/yellow parameter b* also changed remarkably: the undoped VO₂ sample showed a positive value, indicating a stronger yellow colour, while the W-doped one showed a negative value, characteristic of a blue colour.

**DISCUSSION**

Previous work published on tungsten-doped VO₂ thin films utilising a system of VOCl₃, WCl₆ and water gave films with a transmission of ~ 11% at 570 nm [26]. In the previous
work performed using VCl$_4$ as the vanadium source [27] with tungsten(VI) ethoxide and water coreactants, unpredictable results were obtained with films containing variable mixtures of VO$_2$ and V$_2$O$_5$ as observed by XRD, and the maximum visible transmission reported was approximately 40% at 570 nm. Control of film thickness was lacking, which is critical for optimising optical transmission whilst maintaining optimum functional properties, and therefore despite having the characteristic functional switch required the films were inherently unsuitable for application in architectural glazing due to the low optical transmission caused by excessive thickness. In this work, however, a previously unreported system of VCl$_4$/WCl$_6$/H$_2$O was used with a diluent nitrogen flow five times greater than those previously employed [26, 27]. This improved the reproducibility of the results; furthermore the use of higher flow rates led to films where VO$_2$ is the only observable phase (XRD), and V$_2$O$_5$ is only detectable in significant quantities at the film surface (XPS). There were also notable improvements in the visual appearance of the film, and coverage of and adhesion to the substrate was greatly improved over that which was seen in previous work [26,27]. Films grown at higher nitrogen diluent flow rates were more transparent (570 nm) and adhesive than those deposited at lower rates. Most likely this was due to the elimination of gas phase nucleation which has been reported as the cause of many blockages and powdery deposits in previous work [26,27]. The use of higher flow rates was also significant in allowing WCl$_6$ to be successfully employed as a tungsten precursor. Previously this precursor has been used at high bubbler temperatures (240 °C +) [26], and with the deposition equipment used it is virtually impossible to keep all of the material in the gas phase, i.e. preventing blockages, without losing control of film thickness, as witnessed by the deposition of relatively thick films and consequent lower visual transmission. By using higher flow rates the bubbler temperatures can be lowered, whilst maintaining control of film thickness and eliminating blockages.
A linear relationship between the level of tungsten doping and the $T_c$ has been reported previously with an approximate 20 °C change per 1% tungsten doping [31]. However, this was measured only up to 3 atom% tungsten-doping, whereas in the current work the change in $T_c$ was found not to extrapolate in the same linear fashion above 3.5 atom% tungsten doping. Table 2 indicates that the relationship between tungsten doping and $T_c$ appears to be linear up to 3.5 atom% tungsten-doping, with an approximate 22 °C change per atom% tungsten, similar to that seen in previous research. Above this level of doping each atom% of tungsten leads to a change in $T_c$ of 2 °C. There are two possibilities as to why this is occurring. The first is that the tungsten is approaching its solubility limit in the vanadium dioxide. If this were the case we would expect to see evidence of some tungsten metal or tungsten oxide in our characterisation results. However, there is no evidence of any secondary phase in our XRD (Figure 3.) or XPS (Figure 4D.) analysis. Nor is there any evidence of a tungsten oxide phase from Raman spectroscopy (Figure 5.). The second possibility relates to the crystal structure distortion associated with tungsten doping that disrupts vanadium pairs and lowers $T_c$ [19-21]. We suggest that the tungsten doping reaches a critical level that causes the optimum distortion to the crystal structure, and that above this level additional doping has a much less significant effect; because the crystal structure has become so distorted that there is space for additional tungsten atoms to be incorporated without causing as significant a distortion. The switching temperatures at high tungsten loading reported here are the lowest that have been reported for a doped VO$_2$ film.

Films suitable for use in architectural glazing would maximise the functional properties of the coating whilst having a high transmission at 570 nm, preferably in excess of 60% [23]. The thermochromic properties of VO$_2$ thin films are dependent on thickness, the largest changes in optical properties are seen above a critical thickness of 70 nm [14]. The
ideal film would have the maximum acceptable thickness which corresponds to the minimum acceptable optical transmission. In our case this is in the range 70 – 90 nm thick. Also the film must be adherent and visually appealing.

Films deposited with a VCl$_4$:H$_2$O ratio of 1:3 produced glassy, adherent films with the added benefit of having a more appealing green tint in transmission. At this reactant ratio there was no appreciable reduction of the functional properties of the film. For the film to be useful, the thermochromic transition needs to be reduced to around room temperature. From the precursor set used in this work a tungsten doping level in the range of 1.6 – 1.7 atom% would achieve this. Optical properties typical of an optimised film of 80 nm thickness with tungsten doping of 1.66 % are presented in Figure 6. Three temperature regimes were employed; hot (35 °C), room temperature (24 °C) and cold (15 °C). The optical data at 15 °C were partially affected by the condensation of moisture on the film surface during analysis. It is apparent from the data that there is a continued switch in film properties below room temperature, indicating the film is still responding to temperature changes below 24 °C. A large change (50%) in transmission at 2500 nm and a significant change in reflection (20%) is observed between the ‘cold’ and ‘hot’ values. Another significant factor is the colour of the films; previous work has shown that tungsten doped vanadium dioxide films retain the yellow/brown colour of un-doped vanadium dioxide films [14,24-27]. In this work tungsten doping above 2.5 atom% causes the colour to change to a more attractive silver/blue colour. Films with tungsten doping less than 2.5 atom% were greener in colour than had been previously observed; we attribute this to the formation of V$_2$O$_5$ at the surface of the films as seen from XPS (Figure 4A). The formation of V$_2$O$_5$ at the surface is not a new phenomena but in previous studies the films were much thicker (~300 nm) and powdery than those here, which were always glassy, hard and adherent under these conditions, and as such this effect was not observed. We
therefore conclude that this system has the best combination of functional and optical properties, combined with appropriate switching temperature, as required for architectural glazing of any CVD deposited VO\textsubscript{2} thin films.

**CONCLUSION**

Thin films of VO\textsubscript{2}, suitable for use in architectural glazing, have been deposited onto glass substrates using a reliable and reproducible APCVD method. Changing the ratio of vanadium precursor to water alters the appearance of the films from powdery brown to adherent and transparent, with an improvement to a greener colour. This change is also accompanied by a change in the transmission of the films in the near infrared and the size of the MST is dependent on the thickness of the film being above a certain level. Controllable doping of the films with tungsten is demonstrated. This allows the temperature at which the thermochromic switch occurs to be controlled. A benefit of tungsten doping is the films obtain an attractive blue colour in transmission further improving the aesthetic properties.

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**REFERENCES**


List of Figure and Table Captions.
Figure 1. Transmission and reflection spectra at room temperature and 80 °C for 30-nm, 80-nm and 150-nm thick VO$_2$ films prepared by APCVD of VCl$_4$ and water at a 1:3 ratio corresponding to deposition time of 30, 60 and 240 seconds respectively.

Figure 2. SEM image of W-doped doped 80-nm thick VO$_2$ film formed from the prepared by APCVD of VCl$_4$, WCl$_6$ and water, with a VCl$_4$:H$_2$O ratio of 1:3; temperature of the WCl$_6$ bubbler of 130 °C
Figure 3. X-ray diffraction pattern (below $T_c$) of a 1.5 at.% W-doped 80-nm thick VO$_2$ thin film.
A

B

O 1s

V 2p

Intensity (arb. units)

510 515 520 525 530 535 540

Binding Energy (eV)

C

W 4f

Intensity (arb. units)

30 32 34 36 38 40

Binding Energy (eV)
Figure 4. XPS V 2p and O 1s spectra of the (a) as-deposited and (b) etched surface of 1.5 at.% W-doped VO₂ films and W 4f spectra of (c) 1.5 at.% and (d) 8 at.% W-doped VO₂ films.

Figure 5. Variable temperature Raman spectra of 1.75 at.% W-doped VO₂ film deposited with a tungsten precursor bubbler temperature of 152 °C.
Figure 6. Transmission and reflection data for a 1.75 at.% W-doped 80-nm thick VO$_2$ film at 40 °C, room temperature and 5 °C.

Table 1. Summary of WCl$_6$ bubbler temperature and resultant at.% W-dopant concentration and $T_c$.

Table 2. Transmission and reflection colour co-ordinate data for un-doped and W-doped VO$_2$ films.
<table>
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<th>WCl₆ Bubbler Temperature (°C)</th>
<th>W-dopant concentration (at.%) in film [value (standard deviation)] as measured by WDAX.</th>
<th>Tₑ (°C) [value (error)] as determined by Raman spectroscopy and Infra red hysteresis measurements.</th>
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<tr>
<td>100</td>
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<td>55 (± 5)</td>
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<tr>
<td>110</td>
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<tr>
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<td>20 (± 2.5)</td>
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<tr>
<td>177</td>
<td>3.56 (0.71)</td>
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</tr>
<tr>
<td>195</td>
<td>8.20 (0.93)</td>
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Table 1.
<table>
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<th>Tungsten doping (at.%)</th>
<th>Transmission</th>
<th>Reflectance</th>
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<td>Dominant wavelength (nm)</td>
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Table 2