SODIUM TUNGSTEN BRONZE THIN FILMS BY rf SPUTTERING

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ABSTRACT

Polycrystalline Na_xWO_3 films were produced by rf sputtering. Films of low x -value resulted when co-sputtering WO_3 on a $\text{Na}_{0.83}\text{WO}_3$ target, and $\text{Na}_{0.83}$ on WO_3 target. Films of high x and of mixed phase were produced by sputtering a powder mixture of Na_2WO_4 and WO_3 on a tungsten target. Of the sputtering parameters studied, the substrate temperature is the most critical with temperatures above 500°C producing films which were cubic in structure with only a small amount of Tetragonal I. The presence of oxygen up to 3% by volume had minimal effect on film quality or x -value. Auger, electron microprobe, SIMS, SEM, x-ray diffraction, and sheet resistivity techniques were used in characterizing these films. Resistivity of the films was a factor of 10 higher than the bulk crystalline data for $\text{Na}_{0.83}\text{WO}_3$.

INTRODUCTION

Catalytic activity^{1,2} and electro-chromic effects³ have been observed in single crystal sodium tungsten bronzes-- Na_xWO_3 . Since these effects are mainly a surface phenomenon, films of Na_xWO_3 would provide a means of obtaining larger surface area, with the possibility of including different dopants and amounts of dopant into these films than is normally possible in crystal growing methods.

The work reported here investigates the possibility of using rf sputtering techniques to produce films of Na_xWO_3 . Some characteristics of the films were investigated in particular the chemical composition and the electrical resistivity. The effects of the sputtering parameters on the x-value of the films were also investigated.

Thin films of Na_xWO_3 have been produced by Kautz et al.⁴ by serial electron beam evaporation of Na_2WO_4 , WO_3 , and W, with the films then sintered in a vacuum. He found that by this method, single phase polycrystalline tetragonal I sodium bronzes could be obtained. In Kautz's method, the x-value was controlled by varying the thickness of the several films.

Materials having a perovskite structure have been successfully sputtered by Fukunishi⁵ working with LiWbO_3 , and Pratt and Firestone⁶ working with BaTiO_3 . Danielson⁷ has dc sputtered bronzes, but the films were not metallic.

SPUTTERING

Sputtering is the removal of aggregates of atoms by particle impact; the particle used in dc and rf sputtering generally is an ion. Sputtering was long regarded as a thermal spike or "hotspot" phenomenon,⁸ with the energy of the incident ion heating a small volume as it slowed down in the lattice. The heating resulted in evaporation of the material at the point of impact for a short time - until the heat diffused away. When Wehner⁹ discovered preferential directions of ejection from sputtered single crystals, the "hotspot" idea was changed to a momentum transfer mechanism. Momentum is transferred from the incident ion to the lattice, causing ejection of material from near the surface of the target. In single crystals there is an equal effect from focused collisions.^{10,11}

The first reporting of rf sputtering was by Robertson and Clapp in 1933.¹² They observed that material was removed from the walls of a glass tube if it was subjected to a high frequency discharge through external electrodes. In 1962, Anderson et al.¹³ showed that by applying an rf voltage to the outside glass wall of a thermoionically supported sputtering system, the inside of the wall was cleaned. They suggested that this method could be used for the deposition of insulating films. Davidse and Maïssel^{14,15} developed Anderson's general approach into a practical method for the deposition of insulating films at reasonable rates. They also showed that a triode system was not necessary and that apparatus resembling a dc sputtering system could be used. Details about rf sputtering are included in the appendix.

Although sputtering is known as a "dirty process," the presence of reactive gas is sometimes beneficial. Using a reactive gas as or with the sputtering gas is known as reactive sputtering. Mechanisms for reactive rf sputtering are given by F. Shinoki and A. Itoh¹⁶ and Abe and Yomashina.¹⁷ Whether the reaction takes place at the sputtered film or at the target is determined by the partial pressure of the reactive gas. If the pressure is less than a critical pressure, the reaction will occur at the substrate - gettering all the gas - leaving none for target reaction. At pressures above the critical pressure there is sufficient reactive gas to react at the target, thus sputtering the reacted material. Questions exist as to whether the reaction occurs in the dark-space instead of at the target surface.¹⁸

RESISTIVITY

Four probe resistance measurements were made using two different probe configurations - a Van der Pauw square probe array and sputtered contacts.

Wieder¹⁹ has recently reviewed the Van der Pauw method for electrical and galvanomagnetic measurements on thin films and epilayers. He gives the resistivity for an asymmetric probe arrangement of the Van der Pauw type to be (here probe contacts are numbered clockwise):

$$\rho_{12} = \frac{V_{12}}{i_{43}} \frac{\pi D}{\ln(r_{24}r_{13}) - \ln(r_{23}r_{14})}$$

where V_{12} is the potential difference between electrodes 1 and 2, i_{43} is the current applied between electrodes 3 and 4, the r_{ij} terms represent the actual distance between corresponding electrodes, and D is the film thickness. If one finds the resistivity in two perpendicular directions, i.e. ρ_{12} and ρ_{14} , and if $\bar{R}_{12} = \frac{1}{2}(V_{12}/i_{34} + V_{21}/i_{43})$ and $\bar{R}_{41} = \frac{1}{2}(V_{14}/i_{32} + V_{41}/i_{23})$, then the average sheet resistivity should be affected little by electrode contact problems. The average sheet resistivity $\bar{\rho}$ is then:

$$\bar{\rho} = \frac{\bar{\rho}_{12} + \bar{\rho}_{14}}{2} = \frac{1}{2} \left(\frac{\bar{R}_{12} \pi D}{B_{12}} + \frac{\bar{R}_{41} \pi D}{B_{14}} \right)$$

where B_{12} is $(\ln(r_{13} r_{24}) - \ln(r_{23} r_{41}))$, B_{14} is $(\ln(r_{13} r_{24}) - \ln(r_{34} r_{12}))$. The probe spacings vary from sample to sample because the contacts are

spring loaded. Since these variations can introduce up to 3% difference in B_{ij} , measurements of possible probe spacing were made and the average values of $\bar{B}_{12}$ and $\bar{B}_{14}$ were used. The resistivity can be written as:

$$\bar{\rho} = \frac{\pi D}{2\bar{B}_{12}\bar{B}_{14}} (\bar{R}_{12}\bar{B}_{14} + \bar{R}_{14}\bar{B}_{12})$$

In the bridge method, metal contacts are sputtered on to a rectangular section of film. Given the current through the sample and the voltage between the voltage contacts, the resistance of the volume between voltage contacts can be found. Resistivity is

$$\rho = \frac{V}{I} D \left(\frac{W}{L} \right)$$

where D is the film thickness, W is width of the sample, and L is the distance between the voltage probes.

COMPOSITION

X-ray diffraction work by Hagg²⁰ on Na_xWO_3 has shown that the lattice parameters vary with x-value, expanding or contracting to accommodate the sodium variation. A structure change also occurs in the Na_xWO_3 lattice, going from cubic for x greater than 0.48, to tetragonal when x is 0.48 to 0.25 with $c/a = 0.3$ (designated tetragonal I), and then to another tetragonal structure (designated as tetragonal II), when x is 0.25 to 0.05. All the possible compounds of sodium, tungsten, and oxygen which have been studied by x-ray diffraction are listed in Table I. Table I illustrates the differences existing in crystal plane spacing (d-spacing) for different sodium tungsten compounds.

Two x-ray techniques were used in this investigation. With a Norelco x-ray diffractometer, strong peaks were obtained and the crystallinity of the films was ascertained. The substrate and Na_xWO_3 film were placed at the axis of the diffractometer with no special sample modification necessary. An uncertainty of $0.05 \text{ \AA}$ in the d-spacing measurements is not unreasonable due to sample alignment and other operational errors. In using the Debye-Scherrer camera, destruction of the film was necessary.

Another physical property of the bronzes which changes with x-value is the color of the material. There are discrepancies in the color to x-value relationship; Table 2 gives two color schemes for the sodium tungsten bronzes.

Table 1. d-spacing of possible compounds of sodium, tungsten, and oxygen.

Compound Structure ASTM card No.		Main d-spacing Å			
NaWO ₃ Cubic	(5-367)	3.862 _x ^a	2.730 ₈	2.234 ₂	1.931 ₅
		1.728 ₃	1.577 ₃		
Na ₁₀ WO ₃ Tetragonal II	(5-389)	3.89 ₉	3.70 _x	3.12 ₈	2.68 ₉
		2.62 ₉	2.17 ₉	2.00 ₆	1.94 ₃
		1.85 ₉			
Na ₂₈ WO ₃ Tetragonal I	(5-361)	6.04 ₁	5.41 ₇	4.27 ₃	3.82 _x
		3.74 ₉	3.35 ₈	2.93 ₈	2.67 ₉
		2.50 ₇	2.31 ₇	2.19 ₅	1.702 ₆
		1.555 ₇			
Na ₂ WO ₄ Cubic	(12-772)	5.28 ₉	3.23 ₉	2.753 _x	2.282 ₁
		2.094 ₂	1.8642 ₄	1.614 ₄	1.543 ₂
WO ₃ Monoclinic	(15-363)	3.835 _x	3.762 ₉	3.642 _x	3.411 ₅
		3.342 ₅	3.109 ₅	3.076 ₅	
WO _{2.9}	(5-0386)	3.74 _x	2.65 ₃	2.200 ₃	3.10 ₂
		2.02 ₁	1.88 ₃	1.78 ₁	1.67 ₆
		1.53 ₅			
W ₁₈ O ₄₉ Orthorhombic	(5-392)	4.43 ₂	3.78 _x	3.63 ₆	3.44 ₆
		3.39 ₅	2.91 ₄	2.654 ₆	2.620 ₅
		2.522 ₅	1.888 ₇		
WO ₂ Monoclinic	(5-431)	4.78 ₂	3.45 _x	2.828 ₂	2.436 ₆
		2.418 ₈	1.724 ₇		
Na ₂ O Cubic	(3-1074)	3.19 ₄	2.76 ₄	1.95 _x	1.67 ₁
		1.60 ₂			

^aSubscript indicates relative intensity. x=10

Table 1. (continued)

Compound Structure ASTM card No.		Main d-spacing Å			
Na_2O_3	(16-270)	3.79 ₉ 1.897 ₅	3.09 ₄	2.885 ₄	2.095 _x
$\text{Na}_2\text{W}_4\text{O}_{13}$	(15-494)	8.11 ₉ 3.48 ₉	6.12 ₂ 2.728 ₄	4.06 _x	3.78 ₉
$\text{Na}_2\text{O}(\text{WO}_3\text{H}_2\text{O})_{8-40}$ (17-616)		6.40 ₄	3.90 ₇	3.18 _x	2.463 ₅

Table 2. Color and lattice constant variations in Na_xWO_3 .

x-value	Color ^a	Color ^b	a_o^c
0.90	golden yellow		3.859
0.80	yellow	yellow	3.850
0.65	orange-red	red	3.838
0.60	red	violet	3.834
0.45	red-violet	blue	3.821
0.35	blue-violet	blue	3.814
0.32	dark blue-violet	blue	3.811

^aFrom Hagg.²⁰^bFrom Atoji and Rundle.²¹^cCalculated from equation $a_o = 0.0818 x + 3.785$ - Wechter et al.²²

The major chemical analysis was done using an Applied Research Lab Model EMX electron microscope. The amount of sodium and tungsten present in the films was reported in weight percent using a piece of the bronze target crystal as the reference standard. Using the ratio of sodium weight percent to tungsten weight percent (Na wt/W wt) for each film and the tungsten data for the M x-ray line, the x-value is $8(\text{Na wt/W wt})$. Here, 8 is the atomic ratio of tungsten to sodium. The microprobe equipment also monitors the current through the sample, thus giving a conductivity image of the part of the film being analyzed. Contaminates having an atomic number greater than 10 can also be detected in the film.

Two other compositional techniques, Auger and SIMS, were used. The PHI Auger system is capable of only qualitative analysis due to calibration problems. Since the depth of analysis is only a few monolayers, reference standards are difficult to obtain. This technique gives information about only the surface and none about the bulk of the film. A 3M Secondary Ion Mass Spectrometer was used to investigate the chemical homogeneity of the films. The system has a rasterable ion beam, making possible one element composition profiling of a surface area. The sensitivity to sodium is on the order of parts per billion.

A scanning electron microscope was used primarily to investigate the surface structure differences of the films. Since sample current is the display, any conductivity variation in the film gave coloration to parts of the film with no surface structure actually being present. Thus,

coloration changes can give an indirect method of measuring electrical inhomogeneity. Thickness measurements were also made using the SEM equipment.

EQUIPMENT

The sputtering system consists of an Ion Equipment Corporation sputtering module having three 15 cm diameter water-cooled targets and having etch and rf bias sputtering capabilities.²³ Figure 1a is a block diagram of the sputtering vacuum system and gas monitoring equipment. Figure 1b shows the rf circuitry of the sputtering module. The sputtering power was supplied by an rf generator at 13.56 MHz with power capability of 1 kW. One target was replaced by a variable temperature substrate holder²³ capable of maintaining temperatures from -150°C to 600°C . The target dark shield had a 5 cm diameter opening, thus exposing a 20 cm^2 area of the target for sputtering. The substrates were held to the surface of a 6.35 mm thick copper plate mechanically secured to the substrate holder by an aluminum mask. Sputtering temperatures were measured with a chromel-alumel thermocouple in the substrate holder.

Figure 2 is a drawing of the Van der Pauw holder used in the resistance measurements. The probe was made of lavite with copper electrodes, which were held to the surface of the film with 10 mil tungsten springs. A chromel-alumel thermocouple was silver soldered to the bottom of the copper holder. The data was taken during heating and/or cooling in non-equilibrium temperature conditions. The temperature variation for the bridge resistivity measurements was obtained by using a thermoelectric cooler system reported by Kulkarni.²⁴ Figure 3 shows the contact configuration sputtered on to the sample. Electrical contacts were made

Figure 1a. Block diagram of the sputtering vacuum system and gas monitoring equipment.

Figure 1b. Rf circuitry of the sputtering module.

Figure 2. A drawing of the Van der Pauw holder and probe used for resistance measurements. Section A-A shows the electrical contact configuration; distance between the contacts is 11mm. The drawing is not to scale.

Figure 3. Contact configuration used for the bridge method measurements. The substrate is a 12.7 mm square, with a molybdenum contact thickness of 7 μ m. The sample is a 8 mm x 2.5 mm rectangle.

Figure 4. Block diagram of circuitry used for resistivity measurements. The voltage probe selection switch selects the contact configuration.

to the molybdenum pads with phosphorus bronze electrodes. A block diagram of the measurement circuitry is given in Fig. 4. Leeds and Northrup K-3 universal potentiometers and Leeds and Northrup D-C null detectors were used to make all voltage measurements.

Although several different targets were used, the main target was made from a large crystal, 2.5 cm x 2 cm x 3 cm, of $\text{Na}_{0.83}\text{WO}_3$.²⁵ This crystal was slabbed into 2 mm thick pieces which were then bonded to a stainless steel plate, 14 cm in diameter, with Eccobond Solder 59 epoxy in a mosaic pattern to form a 56 cm² area target. The dark shield, as modified, covered all but the center 20 cm² of this target. The bronze target was also used in co-sputtering runs with WO_3 or low x-value bronze powder placed over part of the target surface. Another target used was of tungsten oxide, 15.4 cm in diameter, with $\text{Na}_{0.83}\text{WO}_3$ islands placed on the target surface. The oxide target was permanently bonded to a demountable stainless steel plate with Eccobond Solder 59 epoxy. The target was not WO_3 but reduced slightly during fabrication to about W_2O_5 . Tungsten metal was bonded with Eccobond Solder to a 14 cm diameter plate, and then covered with sodium tungstate (Na_2WO_4) and a small amount of WO_3 . The target thus formed should be analogous to that used in the Kautz et al.⁴ method.

The substrates were standard 1.3 cm x 1.3 cm x 0.08 cm Corning 7059 glass with typical surface smoothness of one-half microinch (manufacturer's figure). The substrates were cleaned by blowing the dust

and lint off with canned air, or by washing in a hot saturated sodium hydroxide solution and then rinsing with distilled water. The two methods were equivalent except that the latter gave fewer pinholes.

For bridge measurements, molybdenum contacts were sputtered onto the films to provide electrical contacts. The bronze films were first sputter-etched for two minutes to rid the surface of contaminants, and then coated with $0.7\text{ }\mu\text{m}$ of molybdenum using a mask. The desired film section was then isolated from the rest of the film by taking off the unwanted or connecting areas with a razor blade. Several samples were prepared by masking of the bronze films but then the square array method was not usable. The W/L ratios for these samples were measured with a traveling microscope.

RESULTS

Films containing sodium and tungsten were obtained with a variety of targets. Table 3 gives the sputtering conditions and the x-values calculated from electron microprobe data for a few of the sputtered films. Several of the films were analyzed with the Auger system but only identification of contaminants was obtained. Figure 5 is an Auger spectrum of a bronze film. One can see that the only elements present, aside from typical air contamination, are sodium, tungsten, and oxygen. Electron microprobe also indicated absence of contaminants. The Auger system was not used for x-value determinations due to a change in the Na/W ratio with analysis time and calibration problems. Figure 6 shows the change in Na/W during a thirty minute period.

X-ray diffraction showed the films to be mainly cubic in structure. For crystalline films, a thickness on the order of $1.0 \mu\text{m}$ was necessary to obtain any detectable diffraction peaks with the diffractometer or have enough material to make camera samples. Two spectrums are shown in Fig. 7. One is a debyogram of the lines observed using a Debye-Scherrer camera, while the other is the diffractometer plot. Table 4 gives the d-spacings of three samples and the possible sodium tungsten bronze structures. The peak at $d = 2.08 \text{ \AA}$ indicates that the film is not entirely cubic Na_xWO_3 but contains a small amount of tetragonal I. Calculating the lattice parameter from the Debye-Scherrer camera data gave an x-value²¹ of 0.83 ± 0.02 for the cubic constituent of the film.

Table 3. Sputtering parameters, target configuration, and x-value for selected films.

Sample No.	Target Description	Substrate Material	Substrate Temp. °C	% oxygen by vol.	Calc. x-value
244		7059	20	4.5	.3
253R	Bronze target with small amount of WO_3 on target surface	7059	440	--	.5
253U		7059	470	4.5	.3
340		SiO_2	470	--	.3
304	WO_3 target with $\frac{1}{2}$ coverage of bronze islands	7059	410	1.6	.4
314		7059	570	--	.4
332	WO_3 target-- $\frac{1}{4}$ coverage bronze	7059	400	1.6	.1
350	Bronze target-- $\frac{1}{4}$ coverage $Na_{0.16}WO_3$	SiO_2	20	--	.1
64B	Bronze target	7059	430	--	.5
733	$Na_2WO_4 + WO_3 + W$ target	7059	500	--	.65
82A	Bronze target	7059	500	--	.55

Figure 5. Auger spectrum of a Na_xWO_3 film indicates the presence of only air contaminants. Sodium-tungsten peak ratio does not indicate the film's x-value.

Figure 6. The sodium-tungsten ratio versus time during Auger analysis of film. The electron beam was 5 kV and 50 μ A.

Figure 7. X-ray diffraction spectrum for sample 64B by two methods. The upper spectrum is from a Debye-Scherrer camera, with the relative intensity of the lines visually estimated. The lower spectrum is a diffractometer chart recording.

Table 4. d-spacing of three sample films obtained with diffractometer and Debye-Scherrer camera compared to possible crystal structure.

hkl	Cubic ^a	hkl	Tetragonal I ^b	Debye-Scherrer Camera			Diffractometer ^c	
	d-spacing		d-spacing	473	68B-53	64B	68B-53	64B
100	3.86	200	6.04	6.58	6.63	6.61	7.02	
		220	4.27	4.12	4.17	4.15	4.30	?
		310	3.82	3.90	3.87	3.88	3.89	3.88
		001	3.74	3.74	--	--		
110	2.73			--	3.45	--	3.49	
		320	3.35	3.28	3.30	3.31		
		420	2.70	2.74	2.74	2.74	2.75	2.73
		321	2.50	--	2.54	2.52	2.54	
111	2.23	401	2.35	2.36	2.37	2.36		
		411	2.31	2.31				
		331	2.27		2.26	2.26	2.28	2.27
		421	2.18	2.20	2.18	2.18		
200	1.93			2.14	--	2.13		
		530	2.07	--	2.07	2.06	2.08	2.08
		620	1.91	1.90	1.94	1.95	1.94	1.93
210	1.73	212	1.78					
211	1.58			1.73	1.73	1.73		1.73
		612	1.70				1.69	
		711	1.56	1.56	1.58	1.58		
220 221,300						1.44		
				1.41	1.41	1.40		
				--	1.36	1.36		
				--	1.29	1.29		
				1.24	1.25	1.25		

^aASTM 5-367.

^bASTM 5-361.

^c473 had no diffractometer peaks.

The same calculation on the target material gave an x-value of $.832 \pm .009$. As Table 5 shows, the x-ray spectrum of sample 733 - prepared using the $\text{Na}_2\text{WO}_4 + \text{WO}_3 + \text{W}$ target - was very different. Listed in Table 5 are the d-spacings of the as sputtered film and the d-spacing of the film after it had been heated for eight hours at 560°C . One can see that this compound best fits the Na_2WO_4 diffraction.

Although electron microprobe detected composition variations across the films, the variations are at the limit of its sodium sensitivity. Secondary Ion Mass Spectrometer, being much more sensitive to sodium, shows in Fig. 8 that the films are not homogeneous in sodium concentration. The three photos indicate the relative concentration at three different raster size settings. The sample current produced by a rastered electron beam impinging upon the bronze films have maxima and minima, implying areas of different conduction. In Figs. 8 and 10 are photos of the sample current observed with both the electron microprobe and SEM.

The surface structure of the films vary widely but all are rough. Figures 9 through 14 are SEM photographs of some film surfaces. The thickness of the films can also be measured with the SEM if an edge has been overcoated with a conducting material. In Fig. 14 are typical photos used in these measurements. The sample was rotated 45° about the x-axis, therefore the actual thickness is 1.41 times greater than the photo indicates - the x-axis scale is not changed in this rotation. The measurements were within 4% of those using a Sloan Dektak.

Figure 8. Upper left, upper right, and lower left are SIMS sodium profiles of a Na_xWO_3 film with decreasing raster size or increasing magnification. The lighter the area, the higher the sodium concentration. Lower right shows the sample current using electron microprobe equipment. Width of the area displayed is about $460\text{ }\mu\text{m}$, the darkest area having the lowest conductivity.

Figure 9. Upper left and right are SEM photos of sample 58E showing film fracturing and surface structure at two different magnifications. Lower left and right are SEM photos of sample 81A at two different magnifications showing the film's surface structure.

Figure 10. Upper left and right are SEM photos showing the sputtered surface structure of sample 78B at two different magnifications. Lower left is SEM photo of the sputtered surface of sample 56B. Lower right is SEM photo of sample 56B after 8 hours of pcst-heating at 510° C.

Figure 11. Upper left is SEM photo of surface structure of sample 58A. Upper right is SEM photo of surface structure of sample 71A. The lower two SEM photos show the surface structure of sample 80A at two different magnifications.

Figure 12. The upper two SEM photos are two different surface areas of sample 80B. Lower left SEM photo shows the surface structure of sample 81A. The surface structure of sample 83B is shown in lower right.

Figure 13. SEM photos of: as sputtered surface of sample 62B-upper left; two different magnifications of surface structure, fracturing, and crystal growth in sample 62B after 22 hours of heating at 450°C -upper right and lower left; and fractures in sample 64B after resistance measurements-lower right.

Figure 14. SEM photos of: upper left-molybdenum coated surface of film 81B after having been scribed to form a step. Film surface is at a 45° angle with respect to the electron beam. Upper right-uncoated surface of 81B at same angle to beam. Lower left - Mo coated surface of sample 80A at same angle to beam. Lower right-uncoated film 80A at same angle.

Table 5. d-spacing of film 733 sputtered from a $\text{Na}_2\text{WO}_4 + \text{WO}_3 + \text{W}$ target compared to possible crystal structure.

Before heating	After heating	$\text{Na}_2\text{WO}_4^{\text{a}}$	NaWO_3^{b} cubic	$\text{Na}_{.28}\text{WO}_3^{\text{c}}$ Tetragonal II	$\text{Na}_{.1}\text{WO}_3^{\text{d}}$ Tetragonal I
5.36	5.36	5.28		5.41	
4.32				4.27	
3.90	3.90		3.86	3.82	3.89
3.26	3.26	3.23		3.35	3.12
2.75	2.87	2.75	2.73	2.93	2.68
				2.67	2.62
2.27	2.26	2.28	2.23	2.31	2.17
				2.19	
1.94	2.05	2.09	1.93		2.00
					1.94

^aASTM card (12-772).

^bASTM card (5-367).

^cASTM card (5-361).

^dASTM card (5-389).

From Table 6, listing the variations in x-value with respect to sputtering parameters, we see that the substrate temperature must be above 450°C to obtain polycrystalline films. At temperatures lower than 400°C , film deposition rates were low with the resulting film being amorphous. Films deposited onto substrates at temperatures between 400°C and 500°C had the tendency to crack and be discontinuous as shown in Fig. 10. Post-heating the films, except for amorphous films, at or below deposition temperatures stabilized the electrical properties but had only minor effects on x-ray spectrum, composition, and surface structure (see Table 7 and Fig. 10). Heating at temperatures above that of deposition caused cracking of the films as shown in Fig. 13. Table 8 lists the sputtering parameters for the films upon which resistivity measurements were made.

Film color corresponded to that reported by Hagg²⁰ - see Table 2. The surface of sample 733 was grey after post-heating, but the material next to the glass substrate was yellow. The red-violet films were invariably blue next to the glass substrate. Amorphous films became more yellow after post-heating. The very low x-value films had a greenish-blue hue if they were not opaque otherwise they were blue.

Resistivity measurements were made on several films with both crystallization and annealing effects observed. Figures 15 and 16 show the typical resistance versus temperature curves obtained for co-sputtered films on heated or cooled substrates. They show annealing with the final curves having a negative temperature coefficient, typical of

Figure 15. Resistance versus temperature for sample 403. Substrate temperature during sputtering was 380°C .

Figure 16. Resistance versus temperature for sample 413. Substrate temperature during sputtering was 20° C.

Table 6. The variation of color, x-value, and d-spacing with temperature treatment for selected films.

Sample No.	Substrate temp. (°C)	Color	Post-heating time(hrs) temp(°C)		x-value ^a	d-spacings ^b		
56A	450	red violet	2	470	.6	4.26 2.53	3.88 2.27	2.73 2.07
56B	450	red violet	-	-	.5	4.29 2.54	3.88 2.27	2.74 2.08
			8	580	.4	4.31 2.52	3.89 2.27	2.75 2.07
57A	190	brown black	-	-	.65	Amorphous. Hump centered at 2.81		
57B	190	brown black	2	470	.6	4.27 2.53	3.87 2.26	2.73 2.07
58A	20	brown black	-	-	.7	Amorphous. No peaks		
58B	20	brown black	2	470	.5	4.27 2.53	3.87 2.26	2.73 2.06
83A	555	red violet	6	325	.55		3.88 2.25	2.74 2.07
88	-150	brown black	1/3 1	560 300	.5	No data available		

^aObtained by electron microprobe.

^bObtained with Norelco diffractometer.

Table 7. Variation of x-value and d-spacing with oxygen content in sputtering atmosphere.

Sample No.	% Oxygen by volume	d-spacing ^a after sputtering (Å)	d-spacing after post-heating (Å)	x-value ^b
64B ^c	0.0		3.88, 2.73, 2.27 2.08, 1.94, 1.73	.56
66B ^d	0.75	3.88, 2.75, 2.30 2.07, 1.93	3.93, 2.76, 2.27 2.09, 1.95	.57
67B ^d	1.4	3.88, 2.74, 2.27 2.06, 1.93	3.92, 2.75, 2.28 2.08, 1.94, 1.73	.48
68B ^d	3.0	3.89, 2.76, 2.27	4.18, 3.88, 2.74 2.26, 1.93, 1.73	.44

^aObtained with Norelco diffractometer.

^bObtained from electron microprobe data.

^cSputtered at 430° C and post-heated at 450° C for 4.5 hours.

^dSputtered at 470° C and post-heated at 510° C for 3.5 hours.

Table 8. Sputtering parameters, x-value, and thickness of selected films.

Sample No.	Sputtering Pres. 10 ⁻² Torr	Parameters Argon flow cc/min	Power watts	Substrate temp. °C	Time hrs.	Thickness 10 ⁻⁶ m	x-value ^a
403 ^b	1.90	55	400	380	0.75	---	.4
413 ^b	3.20	75	400	20	---	---	.3
62B	3.36	78	400	430	0.75	---	.5
64B	3.40	78	410	430	1.00	1.75	.5
78B	2.26	80	405	450	1.33	2.75	.6
80A ^c	2.70	114	500	515	1.33	2.25	.5
80B ^c	2.70	114	500	515	1.33	2.25	.5
81A ^c	2.56	113	500	520	1.00	2.00	.5
81B ^c	2.56	113	500	520	1.00	2.00	.5
82A ^c	1.10	77	500	550	1.25	1.60	.55
83A ^c	1.13	77	360	550	1.50	1.50	.55
863	1.40	80	400	540	1.83	2.25	.55
88 ^d	1.30	82	400	-150	1.00	~.3	.5

^aFrom microprobe analysis using tungsten M line.

^bThe target was WO₃ with bronze island.

^cPost-heated for six hours at 325° C.

^dPost-heated to 560° C for twenty minutes and was above 300° C for one hour.

semiconductor material. Figure 17 shows the change in resistance with temperature for films sputtered at 400°C and exposed to temperatures in excess of 400 degrees during resistance measurements. When post-heating temperatures were greater than 400°C , annealing occurred first, followed by film fracturing. Fracturing can be seen in part of Fig. 9 and 13 also showing crystal formation. Films sputtered at substrate temperatures greater than 500°C gave the most reproducible data, but care must be taken not to exceed 250°C during resistivity measurements. The post-deposition heating was done at 350°C so that only annealing occurred.

The resistances at different temperatures, using the Van der Pauw method, are plotted for the 80 series samples in Fig. 18. Figure 19 shows the resulting resistivity at different temperatures for these same samples. Figure 20 gives the plot of resistivity per thickness of sample (or $R(W/L)$) versus temperature for selected samples using sputtered molybdenum contacts and the bridge method. In Table 9, the resistivities obtained for the 80 series films at 20°C by the above two methods are compared along with the temperature coefficient of resistance. In Table 10, the resistivity and temperature coefficient of resistance of the 80 series are compared to single crystal sodium tungsten bronze.

Figure 17. Resistance versus temperature for samples 62B and 64B. In cooling sample 62B from third heating, the resistance increased rapidly below 150° C.

Figure 18. Resistance versus temperature using Van der Pauw method for 80 series films.

Figure 19. Average resistivity versus temperature for 80 series films using Van der Pauw method.

Figure 20. The plot resistivity per film thickness versus temperature for 80 series films using bridge method.

Table 9. Resistivity and temperature coefficient of resistance for 80 series films using Van der Pauw and bridge methods.

Sample No.	Resistivity $\times 10^{-4}$ ohms cm		Temperature coefficient of Resistivity (ohms cm/ $^{\circ}$ C) $\times 10^{-7}$	
	Method 1	Method 2	Method 1	Method 2
30A	3.35	4.12	1.85	1.85
30B	3.16	4.84	1.86	2.18
31A	3.17	4.68	2.0	2.36
31B	----	5.18	----	2.66
82A	3.57	8.96	2.0	5.44
83A	3.31	4.24	1.85	2.87
863	----	3.76	----	----

Table 10. Comparison of resistivity of Na_xWO_3 films to resistivity of single crystals.

Sample	Resistivity $\times 10^{-4}$ ohm cm	Temperature co- efficient of Resistivity $\times 10^{-7}$ ohm cm/ $^{\circ}\text{C}$
Average for thin films Van der Pauw method	$3.31 \pm 4.5\%$	$1.95 \pm 4.1\%$
Average for thin films Bridge method	$5.11 \pm 31\%$	$2.39 \pm 54\%$
Bronze crystal $x=0.85$	0.19^a	0.68^a
Bronze crystal $x=0.60$	0.41^a	0.83^a
Bronze crystal $x=0.55$	$0.48^b \pm 4.2\%$	-----
Bronze crystal $x=0.45$ Tetragonal I ($\parallel c$)	$1.03^b \pm 7.8\%$	-----
Bronze crystal $x=0.46$ Tetragonal I ($\perp c$)	$3.51^b \pm 6.5\%$	-----

^aShanks.²⁶^bMuhlestein.²⁷

DISCUSSION

As the data shows, sputtering is a viable means of obtaining thin films of sodium tungsten bronze. Variation of film x-value is possible by changing the sputtering parameters and by co-sputtering. Some general trends in the characteristics of the sputtered bronze films are as follows:

1) Co-sputtering of WO_3 with $Na_{0.83}WO_3$ islands results in low Na/W ratios, but the films do contain sodium and are not insulators.

2) Co-sputtering of $Na_{0.83}WO_3$ with islands of WO_3 or low x-value bronze gives moderately low Na/W ratios but because both co-sputtering techniques have low deposition rates, no x-ray data were obtained.

3) Films sputtered from the $Na_{0.83}WO_3$ target onto hot substrates result in films that are by chemical analysis and by color $Na_{0.5}WO_3$. The films are predominantly cubic in crystal structure, showing only small amounts of tetragonal I structure. A lattice parameter fit indicates that the cubic structure is $Na_{0.83}WO_3$.

4) Films deposited onto substrates at temperatures less than $400^\circ C$ are amorphous and are brown-black in color. At cold temperatures, approximately $-150^\circ C$, deposition rates and Na/W ratios are low. The highest deposition rate was obtained at about $450^\circ C$.

5) The $W + Na_2WO_4 + WO_3$ target gave a high Na/W ratio but the film could not be identified as a bronze with x-ray diffraction.

6) During bombardment with a non-scanning electron beam, the Na/W ratio decreases - this is observed by Auger analysis and by the electron microprobe.

7) Although the color of 1 μm thick films was accurate in indicating x-value range, exposure to air caused a color change resulting in the red-violet films becoming yellow-brown. The red-violet color returned upon washing with dilute NaOH.

Fracturing of the films arises from two different effects. At temperatures above 400°C , crystallization occurs reducing the volume of the film due to the increased ordering of the atoms in the lattice. The other effect is the mismatch of the thermal expansion coefficients of film and substrate. According to Rosen *et al.*,²⁸ the thermal expansion coefficient for all Na_xWO_3 bronzes decreases sharply (by a factor of 2) at about 200°C . No common substrate material will match the transition in the Na_xWO_3 expansion coefficient.

The resistivity of the films differs from bulk cubic bronze by a factor of 10, but this difference can be explained in several ways. Since the films are polycrystalline, there are many crystal boundaries to scatter electrons - resulting in a larger ρ . Since all the films contain at least two crystal structures, and since the resistivity of the tetragonal structures are much higher than the cubic, the resistivity of the films must be greater than the resistivity of single crystal cubic sodium tungsten bronzes. The deviation in the resistivity using the Van der Pauw method is on the same order as Muhlestein reported in

single crystals.²⁷ Although the films are consistent in composition from sample to sample, as Fig. 8 indicates, the films are homogeneous neither in composition nor in conduction. The inhomogeneity in conduction indicates the existence of constituents of different resistivities. The temperature coefficient of resistance also indicates that there is little sample difference in composition of the 80 series samples. An oxide (tungsten oxide and/or sodium oxide) or a low x-value bronze layer on the film surface will severely affect the bridge method increasing the measured resistivity; whereas the probes in the Van der Pauw method penetrate this surface layer and the resulting resistivity is unaffected.

SUMMARY

A variety of targets can be used in sputtering sodium tungsten bronze films. It is uncertain, however, which is more critical to the Na/W ratio - target composition or the conditions at the substrates. Much more information is needed on the sputtering products and process of sputtering sodium tungsten bronzes. A study of the sputtering phenomenon could readily be done using the SIMS equipment. Bacuvier and Lavellee²⁹ has reported success in cathodic sputtering of powders. He indicated that after approximately five hours sputtering time, the films produced were of the same composition as the target powder. Therefore, by using a powder target, and the powder mixture composition determined by the chemical reaction equation given by Kautz et al.,⁴

one should be able to continuously vary the x-value of the resulting film. Single crystals of bronze could be used as a target, but the resulting films will have a lower x-value unless extra sodium can be added at the substrate.

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APPENDIX: DIODE RF SPUTTERING

If a low frequency alternating voltage is applied to a diode dc sputtering system whose electrodes have equal areas, a dark space will be produced at both electrodes. The system is actually a succession of short-lived dc discharges. The minimum pressure at which the discharge will operate increases as the frequency of the alternating voltage increases from 50 kHz to a few MHz, indicating that there is an additional source of ionization other than the secondary electrons ejected from the electrodes. Electrons can acquire sufficient energy to cause ionization in the glow space as a consequence of their oscillating and making elastic collisions with the plasms in the radio frequency field. Since the applied rf field appears mainly between the two electrodes, an electron which escapes this glow space is lost to the production of ionization. A magnetic field parallel to the rf field will confine the electrons and reduce their chances of leaving the interelectrode space as a result of random collisions. Levitski³⁰ has pointed out that the mechanism by which electrons absorb energy from the rf field will not apply to the heavier ions; thus the heavier ions will be expected to pick up relatively little energy from the rf field. The glow space of an rf discharge develops an appreciable positive potential relative to the two electrodes³¹ with the potential difference appearing across the two dark spaces. This potential difference arises because the electrons have much higher mobility than the ions and are very easily collected

on the electrode whenever it becomes positive with respect to the glow space. This depletion of electrons from the dark spaces results in a rise of the potential of the glow space with respect to the electrodes.

The magnitude of the glow space potential is such that, through most of the rf cycle, no electrons can leave the glow space. Positive ions will be attracted to the electrodes which they will reach after several rf cycles, once they enter a dark space. The rf current through the dark space is thus principally electron displacement current, with only a small fraction being electron or conduction currents. Therefore, to a first approximation, rf coupling across the dark space is capacitive. The majority of the ions that do reach the electrodes have sufficient energy to do sputtering. If one electrode is appreciably larger than the other, the relative capacitive coupling of the glow spaces to the two electrodes changes with the result that the potential of the glow space changes. Since no dc voltage difference can be maintained in the external rf circuit, the dc bias voltages across the dark space at the two electrodes remains equal. Hence, the two electrodes behave as if they are equal in area and material is sputtered at the same rate per unit area from each electrode.

If a capacitor is inserted somewhere in the external circuit, the dc potential differences between the glow space and the electrodes are no longer required to be equal. A rough relationship for the ratios of the dc potential differences between the glow space and the two electrodes can be derived.³¹ If we assume that: (1) the current density of the

positive ions is uniform and is equal at both electrodes, (2) the positive ions come from the glow space and traverse the dark space without making inelastic collisions, and (3) the capacitance across the dark space is proportional to the dark space thickness, the ratio of voltage should therefore be inversely proportional to the ratio of the areas to the fourth power³¹ or $\frac{V_1}{V_2} = \left(\frac{A_2}{A_1}\right)^4$. Since it is usual for one terminal of the rf generator to be at ground potential, the dark shield, the base plate and all other surfaces at ground potential form one of the electrodes. Thus the grounded electrode will be substantially larger than the rf (or target) electrode. If the target is an insulator, the external capacitor is not needed. Figure 21 shows how the discharge can be represented by an electrical circuit. One can also have metallic (or resistive) elements as is indicated in the figure.

Figure 21. The equivalent electrical circuit of a sputtering system during sputtering. If an insulator is being sputtered, the "film" and "target" are capacitive; if the target is metallic, the "film" and "target" are resistive.