Electrocomponent Science and Technology 1980, Vol. 6, pp. 235–240
0305-3091/80/0604-0235 $04.50/0

TANTALUM THIN FILM CAPACITORS WITH VARIOUS TYPES OF COUNTERELECTRODES

G. P. FERRARIS and R. MAY

G. T. E Telecomunicazioni, S.T.Av, 20060-Cassina de' Pecchi, Milan, Italy.

(Received July 15, 1979)

Capacitors have been prepared from N_2-doped, triode sputtered Tantalum films by conventional anodization and photolitographic techniques.

NiCr–Au, Ta–Ti–Pd–Au, Ta–NiCr–Pd–Au have been used as counterelectrode materials and the a.c. and d.c. properties of the capacitors have been compared.

It has been found that a doped Ta thin layer deposited by sputtering between the dielectric and the top electro de does not negatively affect the capacitors characteristics; moreover, a thermal treatment at temperatures as high as 350°C can be tolerated.

If the Ta film deposited after the dielectric formation is used for resistive elements, a fully compatible R–C process is obtained which requires only two vacuum deposition cycles and four photolithographic steps.

1. INTRODUCTION

The possibility of matching very closely the temperature characteristics of thin film Ta capacitors and resistors, makes them a very attractive proposition in high precision, high stability RC circuits. In recent years, capacitor properties have been improved by N_2 doping the Ta base film[1,2,3] at various atomic percentages, giving better yield, temperature and life stability, and lower dissipation factors when compared to first generation capacitors based on pure β–Ta films.[4,5] Moreover, N_2-doped Ta capacitors can withstand exposure to high temperatures, such as those occurring when R and C are obtained on the same substrate: also, thermal treatment can be included in the fabrication process to improve capacitor properties.[4,6,7]

Almost exclusively, NiCr–Au has been used as the counterelectrode metallization, although sputtered NiCr–Pd with subsequent selective gold plating has been used for the counterelectrodes of critical RC active filters.[8]

In the present paper the characteristics of nitrogen doped capacitors with Ta based triode sputtered top electrodes (TaO_xN_y–NiCr–Pd–Au and TaO_xN_y–Ti–Pd–Au) are compared to those of NiCr–Au standard capacitors. The excellent properties of the N_2-doped capacitors are not negatively affected by the presence of the Ta–oxinitride layer at the dielectric interface.

2. PREPARATION OF CAPACITORS AND TEST EQUIPMENT

The Tantalum base electrode films were deposited by triode sputtering from a 60 mm diameter Ta target in a stainless steel, oil diffusion pumped chamber; the sputtering system has been described in more detail in a previous paper,[9] the only difference being the substrate holder, which in the present experiments was of the planetary type, bearing 30 2″ x 2″ square substrates.

Both Corning Glass 7059 and glazed alumina were used and prior to deposition of α–Ta an etch-stop layer of 3000 Å Tantalum pentoxide was reactively deposited onto the substrates in an Ar and O_2 atmosphere. Pure nitrogen was then released in the chamber at flow rates ranging from 0 to 1.6 sccm and, after some minutes of presputtering, nitrogen doped Ta was deposited for 40 minutes at a deposition rate of 110 Å/min. Thickness, sheet resistance, TCR and thermoelectric power were measured on test samples.

Other substrates were processed into capacitors by anodization to 180 V or 230 V in 0.01% wt. aqueous solution of citric acid at room temperature. After reaching the forming voltage, a soak time of 1 hour was allowed for all samples. Photoresist was used to delineate the dielectric pattern during the anodization process.

Different types of counterelectrodes were then sputter deposited onto the substrates in the same triode sputtering system used for the Ta base electrode: NiCr (200 Å)—Au (3000 Å), TaO_xN_y (300 Å)—NiCr (200 Å)—Pd (2800 Å)—Au (3000 Å) and TaO_xN_y (300 Å)—Ti (500 Å)—Pd (2800 Å)—Au (3000 Å). Nichrome was sputtered from a 80:20 NiCr target and Ta—oxinitride was reactively deposited in an Ar—O_2—N_2 atmosphere.

On each substrate, four arrays of 18 capacitors, each 0.1 cm^2 of active area, were patterned by photolitho techniques and some samples were thermally treated at 250, 300, 350°C in air. For voltage step-stress testing and accelerated life tests, leads were soldered on after separating the individual circuits.

Capacitance (C) and dissipation factor (tan δ) were measured with a Hewlett-Packard 4270A automatic bridge at 1 kHz and TCC calculated from values measured at 15°C and 85°C.

Some measurements to establish accurately the dependence on temperature and frequency of C and tan δ were performed with an ESI manual bridge.

For dc insulation resistance measurements, a G.R. 1864 Megohmmeter was employed.

3. EXPERIMENTAL RESULTS

3.1. *Effect of Nitrogen Doping*

The electrical properties of triode sputtered, 4400 Å thick Ta films are summarized in Table I. With no intentional nitrogen doping, the values of ρ = 202 μohm.cm and TCR = −130 ppm/°C can be taken as for a β—Ta crystalline structure. Nitrogen doping at increasing rates first causes the resistivity to fall (65 μohm.cm at 0.6 sccm N_2) and the TCR to rise sharply (+760 ppm/°C at 0.6 sccm N_2). These values are typically referred to a bcc structure. Between 0.6 and 1.6 sccm N_2, TCR steadily decreases to +160 ppm/°C, where a corresponding resistivity of 133 μohm.cm has been measured.

The nitrogen atomic content has not been determined by direct analysis. Because of differences in deposition systems and parameters only a rough estimate is possible from the literature,[6,10] based on TCR and resistivity. The dielectric constant of anodic oxide grown on these films can also be taken into account.

About 15 at % of N_2 has been estimated for Ta films sputtered at 1.2 sccm N_2, from which the capacitors for most experiments described in this paper were obtained.

TABLE I
Electrical properties of N_2-doped Ta films

$F(N_2)$ (sccm)	t (Å)	R_s (ohm/sq.)	ρ (μohm.cm)	TCR (ppm/°C)
0.	3900	5.18	202	−133
0.6	4200	1.51	63	760
0.8	4300	1.75	75	590
1.0	4350	1.99	86	435
1.2	4400	2.27	100	330
1.4	4400	2.66	117	238
1.6	4400	3.03	133	163

The effect of doped Ta composition on capacitor properties has been analyzed for capacitors anodized to 230 V with sputtered NiCr counterelectrodes.

An almost linear decrease of capacitance density has been found with increasing nitrogen in the sputtering atmosphere; this is shown in Figure 1 where the normalized capacitance has been plotted against N_2 flow rate. Dissipation factors and TCC are virtually insensitive to nitrogen doping of base electrodes over the concentration range examined: 2.2 x 10^{-3} and 235 ppm/°C are typical figures, the only exception being nondoped samples which exhibited higher values for both parameters of 3.5 x 10^{-3} and 560 ppm/°C respectively. This is most probably due to temperature rise during sputtering the counterelectrode, as confirmed in a separate experiment where vacuum evaporation was used instead of sputtering.

Different capacitor properties begin to emerge under thermal treatment, as shown in Figures 2 and 3 and the effects of nitrogen content become more

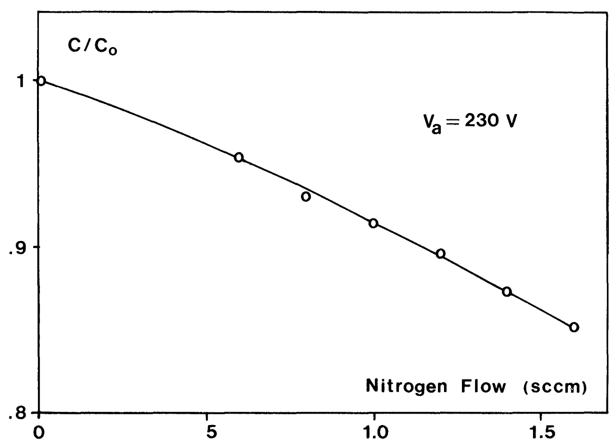


FIGURE 1 Normalized capacitance vs. nitrogen doping of Ta base electrode, anodization voltage 230 V.

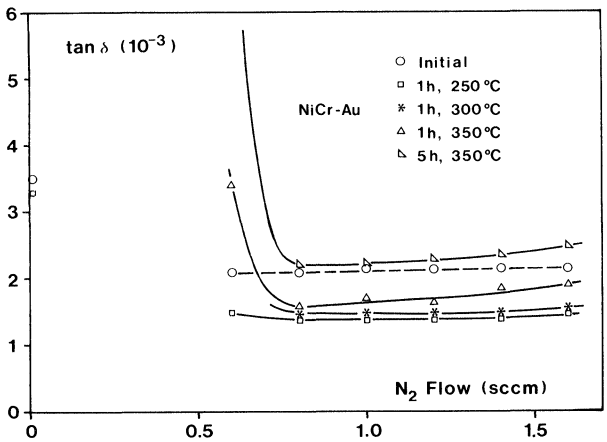


FIGURE 2 Dissipation factor of thermally treated 230 V capacitors with NiCr–Au counterelectrode.

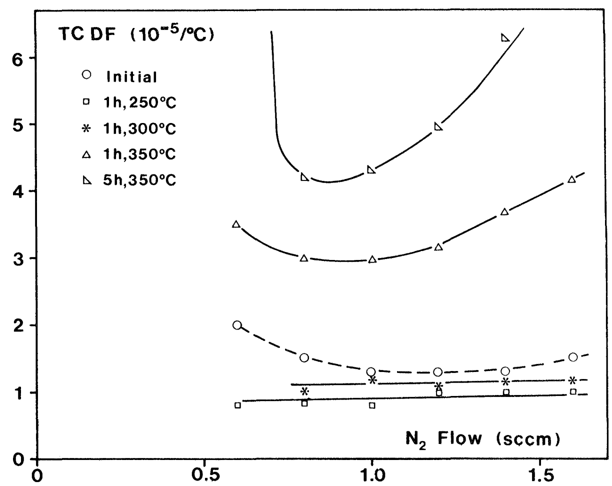


FIGURE 4 Temperature coefficient of dissipation factor between 23 and 85°C of capacitors as in Figure 2.

pronounced as heating time and temperature are increased.

At 250°C for 1 hour, heat treated capacitors show uniform reductions of tan δ and TCC to 1.4×10^{-3} and 150 ppm/°C, regardless of N_2 concentration, and no variations occur after 5 hours.

At 350°C, minimum TCC and tan δ occur between 0.8 and 1.0 sccm flow rate, and both parameters increase with heat treatment time. After 5 hours, capacitors fabricated from low-doped bcc Ta (0.6 sccm N_2) are heavily degraded (TCC = 1100 ppm/°C tan $\delta = 10^{-2}$), while those sputtered at 0.8 to 1.2 sccm N_2 still have a TCC lower than 200 ppm/°C and a tan δ of about 0.0022, showing that they are very resistant to thermal treatment.

The temperature dependence of the dissipation factor has been examined by measurements at 25 and 85°C. In this case also the dependence on nitrogen content becomes evident at the highest stabilization temperature: a minimum value of TCDF = 1×10^{-5}/°C has been observed for capacitors treated at 250°C, while 1 h at 350°C is sufficient to shift this parameter up to 3×10^{-5}/°C (Figure 4).

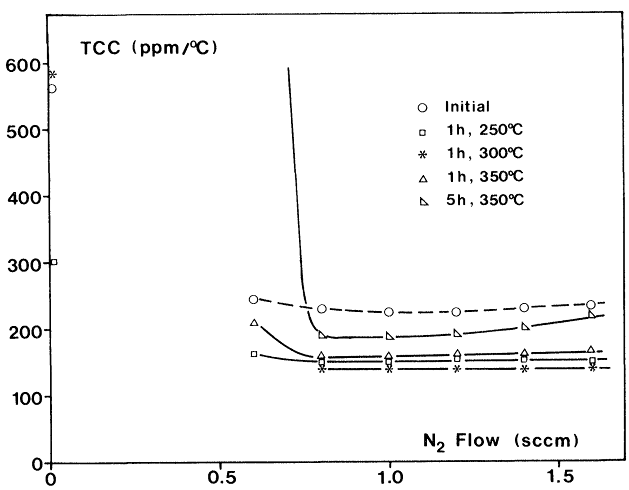


FIGURE 3 Temperature coefficient of capacitance between 23 and 85°C of capacitors as in Figure 2.

3.2. *Effect of Counterelectrode*

Additional substrates were collectively processed by sputtering 4000 Å of α–Ta at a nitrogen flow rate of 1.2 sccm and subsequent anodization at 180 V. These were then split into three groups and capacitors were fabricated with three different types of top electrode, NiCr–Au, Ta–oxinitride–NiCr–Pd–Au, and Ta–oxinitride–Ti–Pd–Au. The Ta–oxinitride layer, about 300 Å thick, has resistivity 330 μohm.cm and TCR –150 ppm/°C. The cumulative distributions of capacitance at 23°C and 1kHz are shown in Figure 5.

The dissipation factor at room temperature is not affected by the structure of counterelectrode employed; mean values of 1.4, 1.6, 1.5×10^{-3} were measured on samples of the three types.

Leakage current is an important parameter to evaluate Ta capacitor quality; 50 V dc was applied with the lower electrode positive and insulation resistance was measured after 30 seconds.

TABLE II
Leakage current measurements

Top electrode	Number of cap.	Number of shorts	Median I_l	90% I_l	Yield $I_l < 2A/F$
NiCr–Au	102	4	0.22 nA	0.5 nA	100. %
TaO_xN_y–NiCr–Pd–Au	120	4	0.5 nA	2. nA	98.3%
TaO_xN_y–Ti–Pd–Au	120	3	0.5 nA	2. nA	100. %

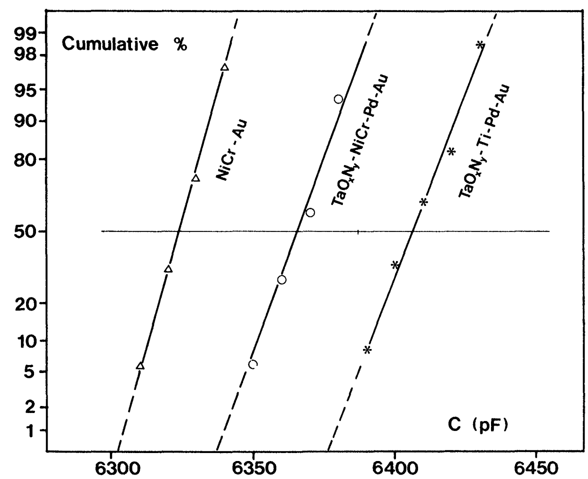


FIGURE 5 Cumulative distributions of capacitance for different types of counterelectrode.

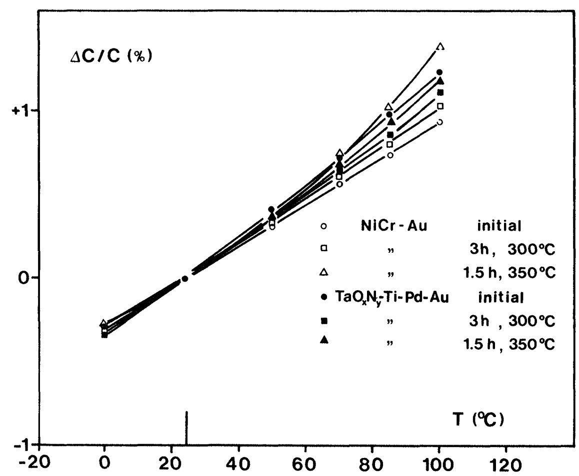


FIGURE 6 Temperature dependence of capacitance for treated and untreated capacitors.

No capacitor with a NiCr counterelectrode exceeded a limiting value of 13 nA except about 4% which broke down under the test voltage. The median value is 0.22 nA.

Leakage currents of capacitors with Ta oxinitride based counterelectrodes are generally higher and more dispersed. No differences were found between Ta–NiCr–Pd–Au and Ta–Ti–Pd–Au, both having a median value of 0.5 nA and this is valid for all electrical parameters considered in this paper.

The results of leakage current measurements are shown in Table II.

The effects of high temperature treatment on capacitor properties can be summarized as follows.

Very small negative capacitance variations, less than –0.15%, are observed for Ta based counterelectrode capacitors which received heat treatment at 300°C, and even after 1 hour at 350°C this type of capacitor exhibited a median capacitance shift of 0.28%, mean deviation of 0.02%. A larger ΔC/C has been measured on NiCr–Au capacitors: 1%, 1.1% and 1.5% for 1 h at 300°C, 3 h at 300°C and 1 h at 350°C respectively.

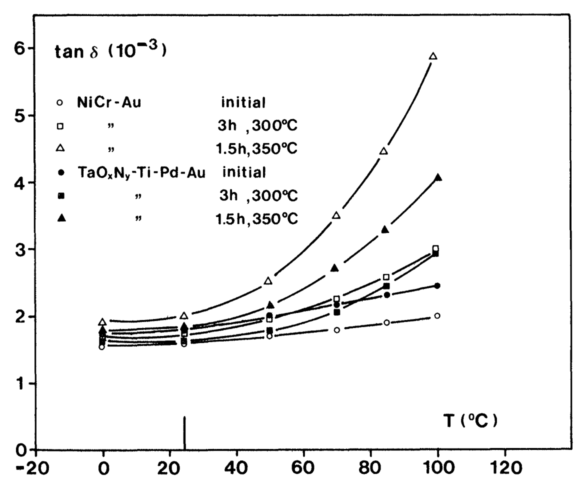


FIGURE 7 Temperature dependence of dissipation factor.

Dissipation factors at room temperature and TCC are consistent at 1.6×10^{-3} and 145 to 150 ppm/°C respectively after 1 hour at 300°C and small variations occur after prolonged treatment. NiCr–Au capacitors show a larger dependence of tan δ on

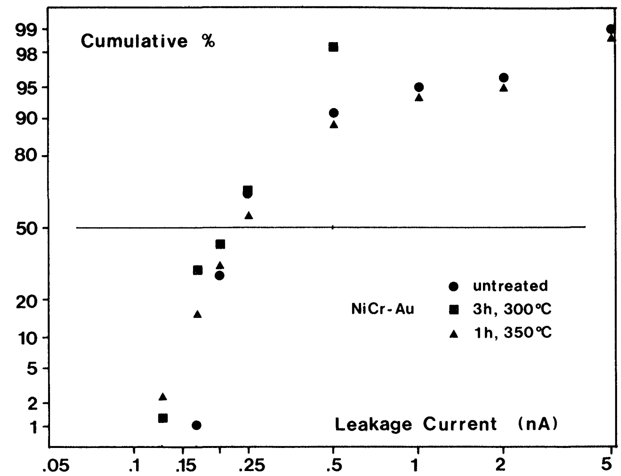


FIGURE 8 Cumulative distribution of leakage current for NiCr–Au counterelectrode capacitors.

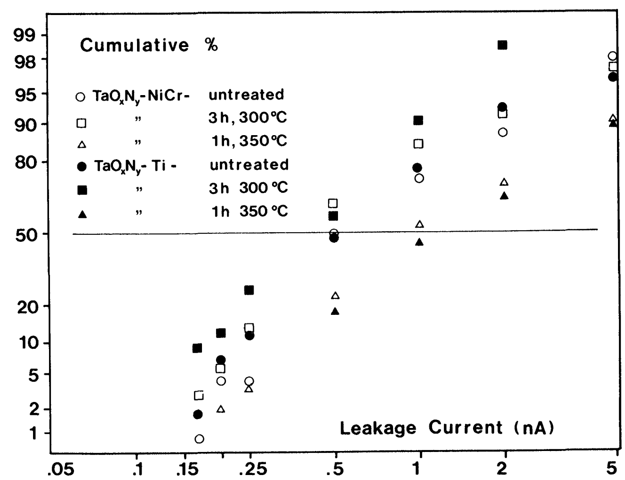


FIGURE 9 Cumulative distribution of leakage current for capacitors with Ta oxinitride NiCr–Pd–Au and Ta oxinitride Ti–Pd–Au counterelectrode.

temperature when heat treated at 350°C, as shown in Figures 6 and 7.

The leakage current of Ta counterelectrode capacitors is somewhat degraded with high temperature treatment, in contrast to NiCr capacitors whose insulation resistance is practically unchanged even after 5 hours at 350°C. This situation is shown in Figures 8 and 9 where the cumulative distributions of l.c. for treated and untreated samples are plotted.

3.3. *Voltage Step-stress Tests*

For preliminary evaluation of capacitor reliability, 12 minute voltage step-stress tests at 85°C were carried out on capacitors with the three types of counterelectrode, before and after thermal stabilization at 300 and 350°C. An important point was to establish whether the leakage current degradation, induced by the thermal treatment on Ta counterelectrode capacitors, yielded lower breakdown voltages and thus potential low reliability.

The distribution of failure voltages for treated and untreated capacitors is shown in Figures 10 and 11.

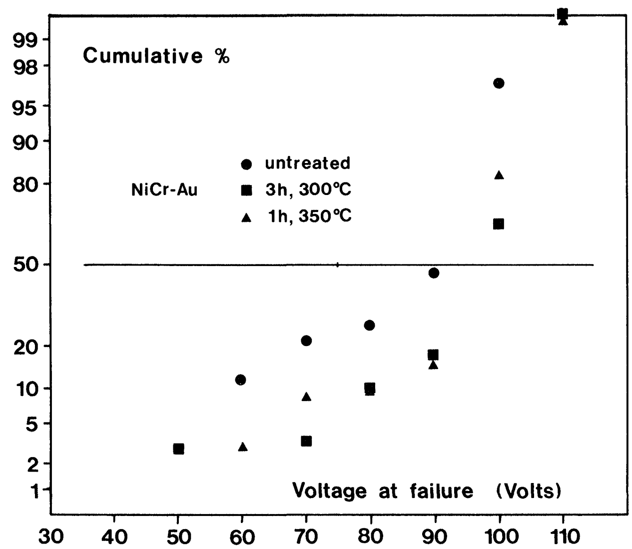


FIGURE 10 Step stress failures at 85°C of NiCr–Au counterelectrode capacitors.

All groups tested exhibit an average break-down voltage of between 90 and 100 V, regardless of the counterelectrode and stabilization treatment; note that unheated NiCr capacitors show the lowest mean breakdown voltage of about 90 V.

These values are comparable to previously published results[3,6] for nitrogen doped, 230 V Ta film capacitors, if the dielectric thickness is taken into account.

D.c. bias accelerated life tests at 85°C are in progress.

Results after 2000 hours with 50 V applied show 8 to 13% failures on 300°C heat treated capacitors, related more to the fabrication lot than to the counterelectrode structure.

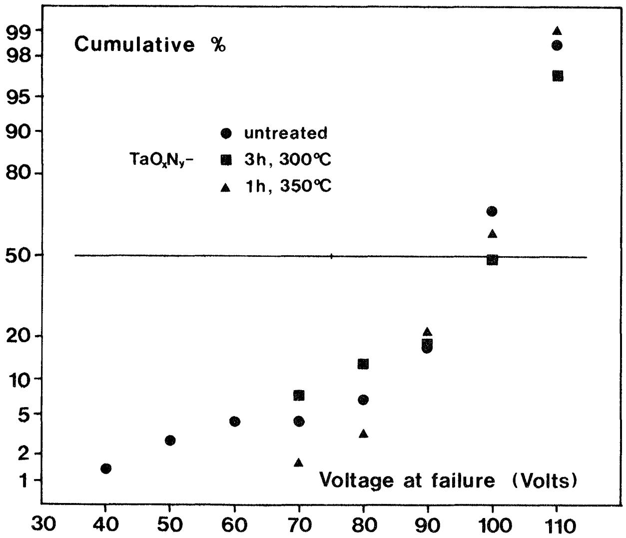


FIGURE 11 Step stress failures at 85°C of Ta based counterelectrode capacitors.

4. CONCLUSION

Capacitors exhibiting excellent a.c. and d.c. electrical properties have been obtained from triode sputtered thin films of nitrogen doped Tantalum.

A Ta oxinitride layer sputtered onto the dielectric and left as a part of the counterelectrode structure does not degrade the capacitor characteristics or their repeatability.

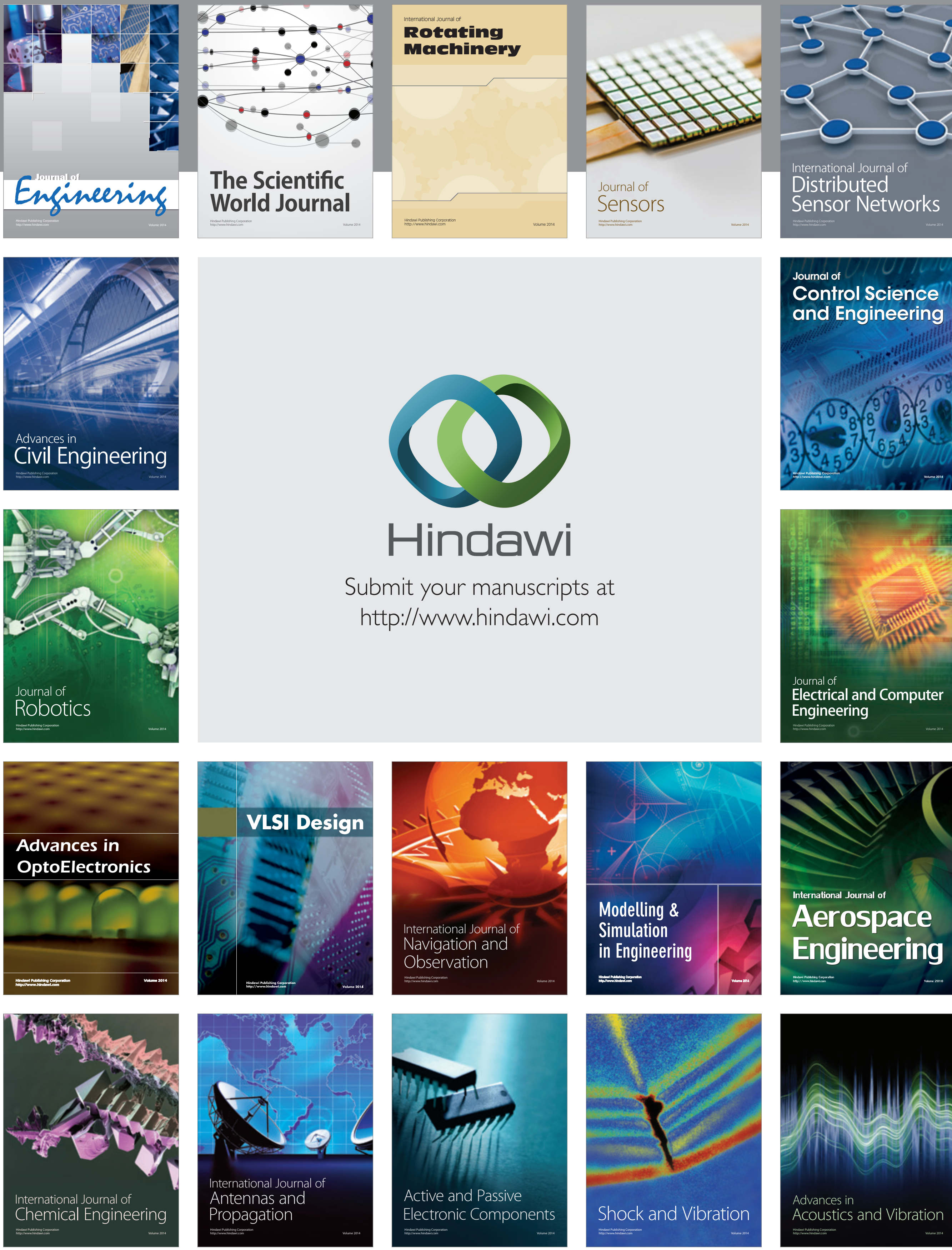
Both NiCr–Au and Ta based counterelectrode capacitors can withstand temperatures as high as 350°C, but optimum results have been obtained by heat treating for 3 hours at 300°C; the temperature stability of the dissipation factor is the parameter most affected by high temperatures. On the basis of these results, the fabrication process of high stability RC circuits can be simplified, in that the capacitors counterelectrodes, resistors and conductors can be obtained from a single multilayer.

ACKNOWLEDGMENTS

The authors wish to acknowledge the assistance of Mr. G. Galimberti, Mr. C. Villa, Miss. M. E. Gironi and the staff of S.T.Av. for their valid help in editing this paper.

REFERENCES

1. H. Y. Kumagay, I. M. Fletcher, C. A. Steidel, K. L. Baurle, and J. R. Hightower, *Proc. 23rd Elec. Comp. Conf.* (1973) 257.
2. W. Anders, *Thin Solid Films* 27 (1975) 135.
3. R. D. Huttemann, I. M. Morabito and D. Gerstenberg, *IEEE Trans.* PHP-11 (1975) 67.
4. R. W. Berry, P. M. Hall and M. T. Harris, *Thin Film Technology* Van Nostrand and Princeton (1968) chapter 8.
5. W. H. Orr, D. O. Melroy, R. J. Moore, F. P. Pelletier, W. J. Pendergast and W. H. Yocom, *Proc. 20th Elec. Comp. Conf.* (1970) 602.
6. M. H. Rottersman, M. J. Bill and D. Gerstenberg, *IEEE Trans.* CHMT-1 (1978) 137.
7. M. Doken, K. Ohwada, S. Okamoto and T. Kamei, *IEEE Trans.* CHMT-1 (1978) 187.
8. R. E. Peterson and K. L. Baurle, *Proc. 27th Elec. Comp. Conf.* (1977) 238.
9. G. P. Ferraris, *Thin Solid Films*, 24 (1974) 113.
10. R. T. Simmons, P. T. Morzenti, D. M. Smyth and D. Gerstenberg, *Thin Solid Films*, 23 (1974) 75.


Journal of Engineering
The Scientific World Journal
International Journal of Rotating Machinery
Journal of Sensors
International Journal of Distributed Sensor Networks
Advances in Civil Engineering
Hindawi
Submit your manuscripts at http://www.hindawi.com
Journal of Control Science and Engineering
Journal of Robotics
Journal of Electrical and Computer Engineering
Advances in OptoElectronics
VLSI Design
International Journal of Navigation and Observation
Modelling & Simulation in Engineering
International Journal of Aerospace Engineering
International Journal of Chemical Engineering
International Journal of Antennas and Propagation
Active and Passive Electronic Components
Shock and Vibration
Advances in Acoustics and Vibration