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THE TEXTURAL EFFECT OF Cu DOPING AND THE ELECTRONIC EFFECT OF Ti, Zr AND Ge DOPINGS UPON THE PHYSICAL PROPERTIES OF IN_2O_3 and Sn-DOPED IN_2O_3 CERAMICS

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The electronic properties of Cu-, Ti-, Zr-, and Ge-doped In_2O_3 (IO) and ITO (Sn-doped In_2O_3) ceramics are investigated. We distinguish the different effect of Cu doping (so called the "textural effect") and of Ti, Zr and Ge dopings (so called the "electronic effect") of IO and ITO ceramics. Indeed, Cu doping in IO and ITO enhances the ceramic density and thereby the conductivity due to an increase in the carrier mobility (grain boundary effect); the absorbance in the visible region is then lowered. Most interestingly for Ti-, Zr-, and Ge-doped samples, the increase of conductivity associated with an enlargement of the electron-mobility along with a decrease of the absorbance in the visible, account for the weak interactions occuring between the conduction-band electrons and the ionized donor centers.

I. INTRODUCTION

Simultaneous high electrical conductivity and transparency in the visible, occuring (i) for undoped but oxygen-deficient In_2O_3 (IO) films or (ii) for Sn-doped In_2O_3 (ITO) films, leads to interesting applications as transparent electrodes and heat mirrors. Hence, numerous researchers have characterized the electrical and optical parameters of such thin films [1, 2]. However, with increasing sophistication of active and passive devices based on ITO thin films, there is still a need for enhancing both the conductivity and the transparency in the visible.

Therefore, an important question arises: "Can the conductivity and the transparency of ITO be improved by doping with appropriate elements?"

In order to thoroughly investigate the effect of doping of IO or ITO film on their electronic properties, it is worthwhile to study ceramics first. Indeed, the ratio of the doping element can be more easily modulated in ceramics than in thin films: Consequently its influence on the electronic properties can be more accurately investigated.

The films also have the same "disadvantages" as the ceramics, such as the relative small size of the grains, which can cause a drop in the carrier mobility (textural effect related to grain-boundary effect). For the above reported reasons, it is more judicious to solve this problem on ceramics first.

Therefore, in the first part of this paper, we will report on the beneficial influence of Cu doping of IO and ITO ceramics on the density accounting for grain-percolation (the "textural effect") and correlate it to the electrical and optical properties. The choice of Cu doping element arises from a previous study on Cu-doped SnO_2 films [3].

In the second part of this paper, we will report on the direct influence of Ge, Zr, Ti doping of IO and ITO on their properties (the "electronic effect"). We have indeed previously reported that Ge doping of IO and ITO samples, either in ceramic or film form, induces a significant enhancement of the carrier mobility and, thereby, of the optoelectronic properties [4, 5]. We will study here Ti or Zr doped IO and ITO ceramics. For sake of clarity this investigation will be carried out on the basis of a comparative study with Ge-doped ceramics.

Although the transport properties of polycrystalline ceramics differs from the intrinsic values obtained on single crystals, the relative values of the charge-carrier

TABLE I
The choice of the doping elements (IO doped samples)

Ceramic symbolization	Starting materials (99.999% pure Alpha prod.)	Cationic doping-elements present	Formation of cond. band el., e^-[C.B.]: examples	"Lewis acid strength" of the doping elements [6]
IO	In_2O_3	None	"active" oxygen vacancies: $In_2O_3 \rightarrow In_2O_{3-x} + e^-[C.B.]_{2x}$	1.03 (In^{3+})
ICO (X)	$xCuO + (1 - x/2) In_2O_3$ (100x = 0.1, 0.5, 1, 2.5, 5)	Cu^+	$In_2O_{3-x} \rightarrow In_2O_{3-y} + [y - x]e^-[C.B.]$	−0.637 (Cu^{1+})
IGO (X)	$xGeO_2 + (1 - x/2) In_2O_3$ (100x = 2)	Ge^{4+}	$In^{3+} \rightarrow Ge^{4+} + e^-[C.B.]$ / e^-[C.B.] from "active" oxygen vacancies	3.06 (Ge^{4+})
IZO (X)	$xZrO_2 + (1 - x/2) In_2O_3$ (100x = 2)	Zr^{4+}	$In^{3+} \rightarrow Zr^{4+} + e^-[C.B.]$ / idem	2.03 (Zr^{4+})
ITiO (X)	xTiO2 + (1 − x/2) In_2O_3 (100x = 2)	Ti^{4+}	$In^{3+} - Ti^{4+} + e^-[C.B.]$ / idem	3.06 (Ti^{4+})
ITO (X)	$xSnO_2 + (1 - x/2)In_2O_3$ (100x = 2)	Sn^{4+}	$In^{3+} \rightarrow Sn^{4+} + e^-[C.B.]$ / idem	1.62 (Sn^{4+})

mobilities versus carrier concentration, n, are generally meaningful for polycrystalline ceramics of the same grain size and density. On the other hand, chemical homogeneity can be more difficult to achieve in single crystals.

The choice of these doping elements is based on the high value of the Lewis acid strength of Ge^{4+}, Zr^{4+} and Ti^{4+} compared to that of Sn4+ [4–6].

II. CERAMICS ELABORATION AND EXPERIMENTAL PROCEDURE

All samples were prepared under similar conditions. Powders obtained by intimately mixing 0.3g of the starting oxides (table I) were cold-pressed in a steel die and then isostatically pressed at 5 tons/cm^2. The pressed pallets were sintered in air at 1300 °C for 24 h after heating to temperature at 100 °C/h: They were subsequently cooled at 100 °C/h.

The structure and texture of the sintered samples were examined by X-ray powder diffraction and by electron microscopy respectively. For Ti, Zr, Ge and Sn doped IO ceramics, the grain sizes (average ca 1 μm) and densities (ca 0.72 theoretical) were all comparable to one another, and there was no evidence of second-phase formation at the grain boundaries for doping content of 1 atomic %.

Accurate values of the conductivity σ, Hall mobility μ, and carrier concentration n, were obtained on polycrystalline plates typically 5 × 5 × 0.5 mm with an A.C. Van der Pauw four probes measurement of σ, a Hall measurement (in a 1.2T magnetic field) of n, and a calculated $\mu = \sigma/ne$. An In-Ga eutectic was used to ensure ohmic contacts.

Optical absorbance measurement upon the same plate samples were investigated in the inter-band and free-carrier absorption regions (the corresponding wavelength is from 300 nm to 700 nm).

III. RESULTS AND DISCUSSIONS

I). Cu Doped IO and ITO Systems

As shown in table II, the density of IO ceramics can be considerably increased by copper doping. This textured effect is in fact very similar to that observed for Cu-doped SnO_2 ceramics: the increase of grain size as the copper content increases accounts for the enhancement of density [3].

For 2.5 (atomic) % Cu-doped IO samples, the density, equals to 7 (table II), is very close to that of single crystals. The average grain size is thus as large as 10 μm. Unfortunately for this composition, there also exists the "impurity" phase CuO, present at the grain boundaries.

From table II one deduces that the higher the sample density, the higher the mobility, and the lower the carrier concentration. The incrase in mobility has to be correlated to the increase in density but not to the decrease in the carrier concentration. Indeed for carrier concentrations of about 10^{18} cm^{-3} as it occurs

TABLE II
Value of Cu doping concentrations in IO and ITO based ceramics; corresponding densities and values of the main electrical parameters.

Starting material ratio	Sample	Density g/cm^3	μ (cm^{2}v^{-1}s^{-1})	n (cm^{-3})	σ (cm$^{-1}\Omega^{-1}$)
In_2O_3 single cristal [7]	0	7.1	160	10^{18}	10
Cu/In = 0	1	4.9	28	2.5×10^{18}	1.12×10
Cu/(In + Cu) = 0.005	2	5.0	40	2.0×10^{18}	1.28×10
Cu/(In + Cu) = 0.25	3	6.0	55	1.7×10^{18}	1.50×10
Cu/(In + Cu) = 0.5	4	6.2	65	1.5×10^{18}	1.56×10
Cu/(In + Cu) = 1.0	5	6.5	80	1.2×10^{18}	1.54×10
Cu/(In + Cu) = 2.5	6	7.0	90	0.8×10^{18}	1.2×10
Cu/(In + Sn + Cu) = 0 Sn/(In + Sn + Cu) = 1	7	4.7	29	1.3×10^{20}	6.03×10^2
Cu/(In + Sn + Cu) = 0.25 Sn/(In + Sn + Cu) = 1	8	4.9	33	1.5×10^{20}	7.92×10^2
Cu/(In + Sn + Cu) = 0.5 Sn/(In + Sn + Cu) = 1	9	5.4	36	1.7×10^{20}	9.79×10^2
Cu/(In + Sn + Cu) = 1.25 Sn/(In + Sn + Cu) = 1	10	5.7	37	1.8×10^{20}	1.07×10^3
Cu/(In + Sn + Cu) = 2.5 Sn/(In + Sn + Cu) = 1	11	6.0	38	1.8×10^{20}	1.09×10^3

here, the main scattering mechanism is due to acoustical phonons, and in this case, the mobility does not depend upon the carrier concentration [8]. However, the mobility always remains smaller than that observed for single crystals (160 cm^2 V^{-1}s^{-1}) [7], although the density is close to the theoretical value: The above mentioned "impurity" phase CuO, present at the grain-boundary, probably introduces Cu2+-related recombination centers, which inhibits the "normally expected" increase in the carrier mobility.

Finally, the decrease in the carrier concentration, deduced from Hall measurements, as the copper concentration increases, would imply that a small amount of copper enters as Cu(I) in the IO lattice, probably in a cationic substitutional position, so that one gets:

$$IN^{3+} + e^- = Cu^+ \quad (1)$$

For Cu-doped ITO samples, the density is also increased by copper doping. However it remains smaller than that observed for IO:Cu; indeed it does not exceed 6 (table II).

On the other hand, and most interestingly, the conductivity of ITO:Cu ceramics is enhanced by copper doping, since both the carrier concentration and the mobility increase as the density increases. In ITO, the free electrons mainly arise from the charge compensation:

$$In^{2+} \longrightarrow Sn^{4+} + e^{-}\ (CB) \qquad (2)$$

From the X-ray diffraction spectra analysis we have deduced that the presence of CuO enhances the solubility of tin oxide in indium oxide ceramics. Therefore, the increase in the carrier concentration with the copper content would mainly arise from the increase of tin solubility in In_2O_3. On the other hand, the effect of grain boundaries is weaker in the heavily doped semiconductors ITO:Cu ($n > 10^{20}$ cm^{-3}) than in IO:Cu as a consequence of the narrower depletion layer width at the interface between two grains. Consequently the increase of density with the copper content does not significantly affect the carrier mobility.

From the optical absorbance point of view, and as shown in fig. 1, the absorbance of IO:Cu samples is dominated by inter-band absorption at high energies; the deduced optical band-energy gap is of the order of 2.8 eV, a value which is currently obtained for ITO [1]. However for heavily doped ITO:Cu samples, the Cu doping induces an enlargement of the band-to-band transition as a consequence of the Burshtein shift effect [9]. For energies lower than that of inter-band transition, the absorbance is mainly due to the free-carrier absorption [10].

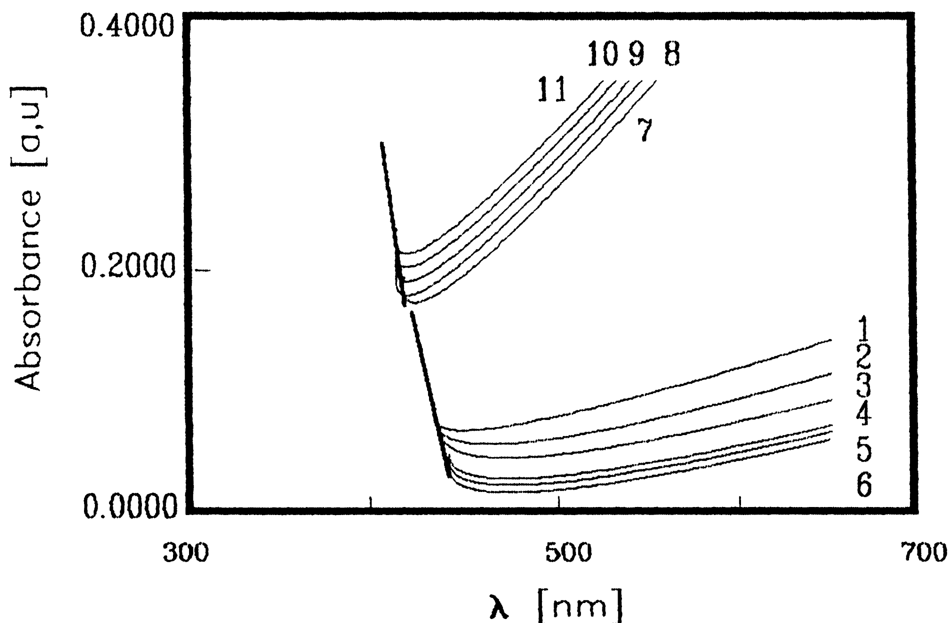

FIGURE 1 Absorbance versus the wavelength for various ceramic samples. The numbers alongside the curves have the same meaning as in table II.

On the other hand, the free-carrier absorption varies with the energy more smoothly for IO and Cu-doped IO than for ITO and Cu-doped ITO because:

(i) in the former case, the scattering takes place mainly on the acoustical phonons as mentioned above; therefore the absorption coefficient a varies with the photon frequency and is proportional to $\nu^{-1.5}$ [11].

(ii) in the later case, the scattering takes place mainly on the impurity ions; therefore the absorption coefficient is proportional to ν^{-3} [12].

II). Ti, Zr and Ge doped IO and ITO systems

For sake of an accurate comparation study we have chosen, for all samples, the same doping concentration, equal to 1 (atomic) %. A decrease in lattice parameters consistent with the smaller size of the dopant (Ti^{4+}, Zr^{4+} and Ge^{4+}) relative to In^{3+} and Sn^{4+} is observed.

Fig. 2 gives, for undoped and Ti; Zr; Ge-, or Sn-doped IO samples with nominal x = 0.01 (table I), the evolution of the room temperature Hall-carrier mobility and carrier concentration as a function of the doping element. Of particular interest

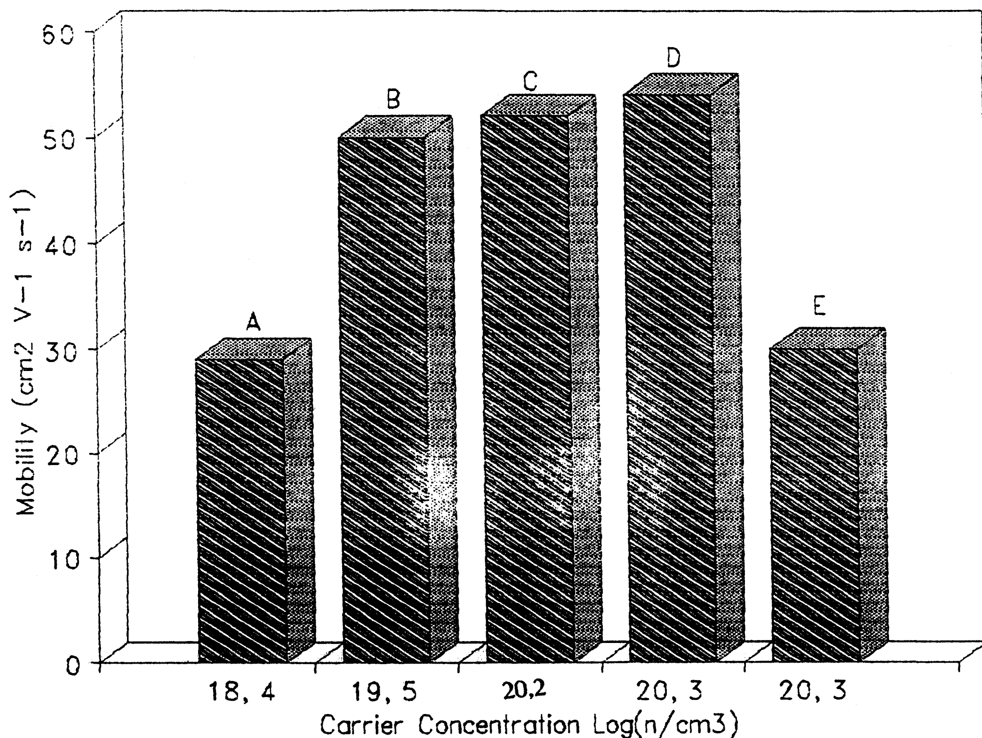

FIGURE 2 Evolution of the room temperature carrier mobility and carrier concentration as a function of the doping elements.
A = IO, B = IZO, C = ITiO, D = IGO, E = ITO.
For all samples: M/(In + M) = 0.01, and here M is Ti, Zr, Ge and Sn.

is the enhanced Hall mobility in Ti-, Zr-, and Ge-doped IO samples compared to that of IO and ITO. We know that in heavily doped n-type semiconductors as it occurs here, the mobility is primarily limited by the scattering of electrons from ionized donor centers. For Ge-doped IO we have previously shown that such scattering would be reduced if the "Lewis-acid strength" of the donor element is higher than that of In^{3+} in IO based semiconductors. A more acidic ionized donor element such as Ge^{4+} would polarize the electronic charge from the $O^{2-}:2p^6$ valence band more strongly towards itself, thereby screening its charge so as to weaken it as a scattering center; consequently the carrier mobility in Ge doped IO is particularly high (fig. 2) [4].

Similar arguments obviously apply for Ti- and Zr-doped IO, since from table I one notices that not only Ge^{4+} but also Ti^{4+} and Zr^{4+} have particularly high "Lewis-acid strength" values.

Finally, and most interestingly, fig. 3 shows the increase in carrier mobility when the "conventional" ITO (Sn/(In + Sn) = 0.01) is doped by Ti, Zr or Ge. These

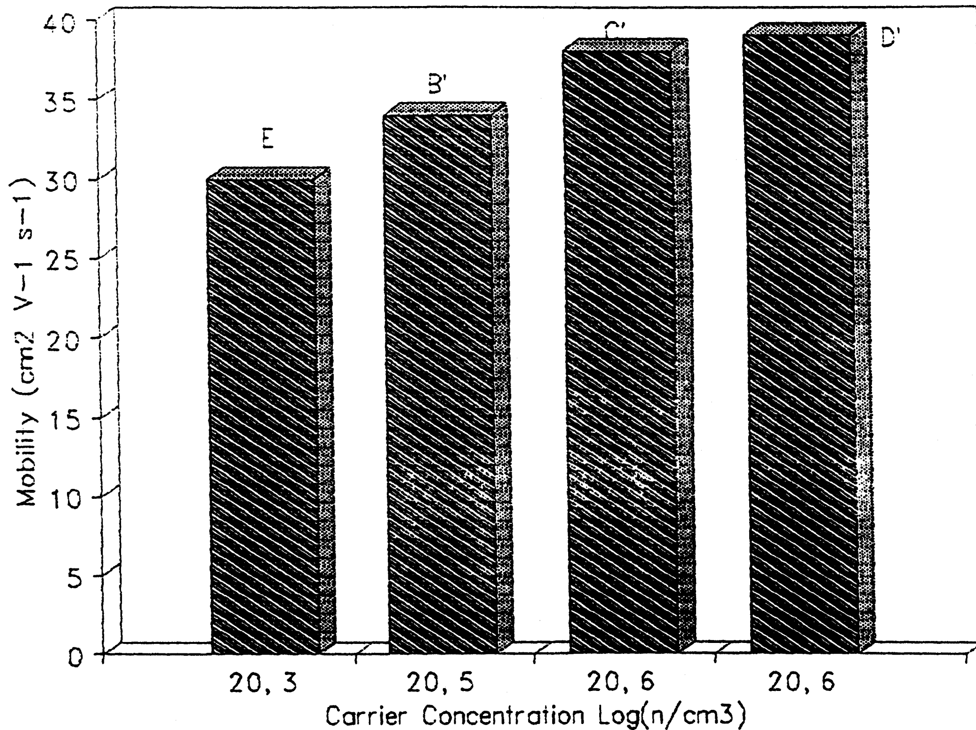

FIGURE 3 Evolution of the room temperature mobility and carrier concentrattion as a function of the doping elements.
B' = ITZO (starting materials: Sn/(In + Sn + Zr) = 0.01, Zr/(In + Sn + Zr) = 0.01).
C' = ITTO (starting materials: Sn/(In + Sn + Ti) = 0.01, Ti/(In + Sn + Ti) = 0.01).
D' = ITGO (starting materials: Sn/(In + Sn + Ge) = 0.01, Ge/(In + Sn + Ge) = 0.01).
E = ITO which has the same meaning as in fig. 2.
The samples symbolization is chosen to be consistent with that of Fig. 2.

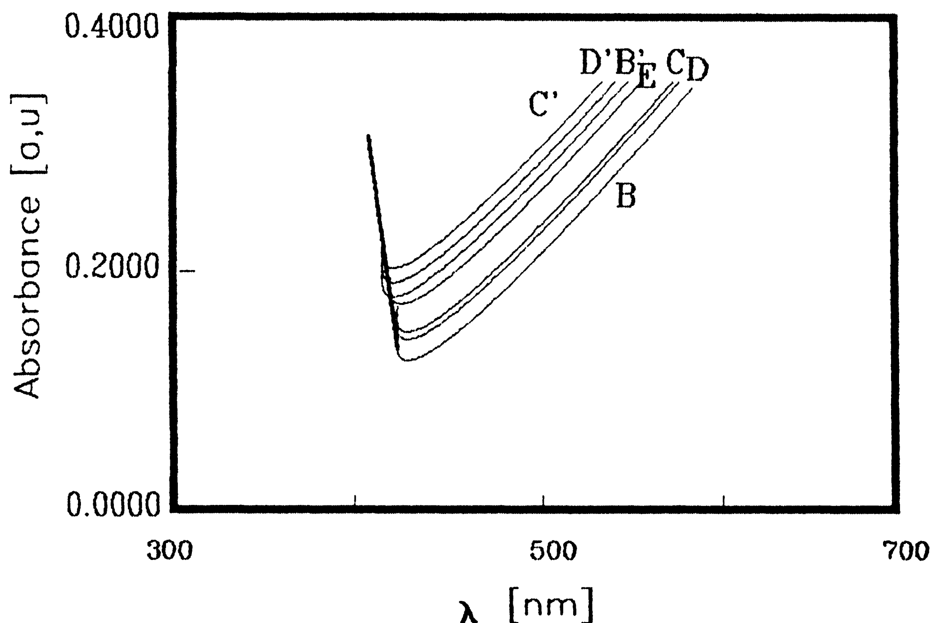

FIGURE 4 Absorbance versus the wavelength for various ceramics. The letters alonside the curves have the same meanings as in fig. 2 and fig. 3.

significant results can obviously be justified on the basis of our above reported arguments.

Fig. 4 gives the optical absorbance of the samples in the inter-band and free-carrier absorption region: the absorbance of Ti-, Zr-, and Ge-doped IO is lower than that of ITO. It means that the Ti-, Zr-, and Ge-doped IO samples in thin film form will be more transparent in the visible than "conventional" ITO films.

IV. CONCLUSION

The electrical and optical properties of IO and ITO can be improved by doping with:

(i) Cu, which modifies the texture by enhancing the density;

(ii) Ti, Zr or Ge because the interactions between the conduction-band electrons and the ionized donor elements are minimized.

In particular, the charge carrier mobility in $In_{2-x}M_xO_3$ (M = Cu, Ti, Zr, Ge) is much higher than that of In_2O_3 and of $In_{2-x}Sn_xO_3$ for x = 0.01. Besides, both the charge carrier mobility and carrier concentration in $In_{2-x-y}M_xSn_yO_3$ (M = Cu, Ti, Zr, Ge) are higher than those of $In_{2-y}Sn_yO_3$ for x = y = 0.01. Finally the Ti-, Zr-, and Ge-doped IO and ITO ceramics are more transparent in the visible than IO and ITO.

Consequently, ITO:Cu, ITO:Ti, ITO:Zr and ITO:Ge would be very good candidates to replace classical ITO. These thin films are presently under investigation.

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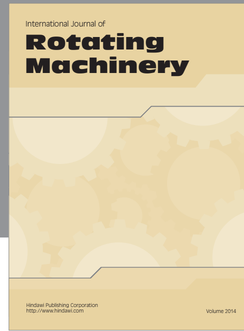
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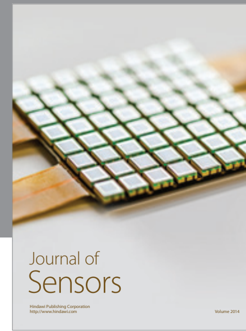
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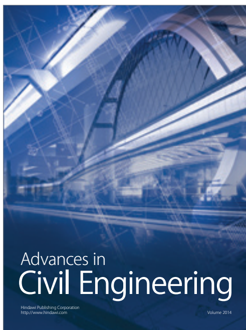
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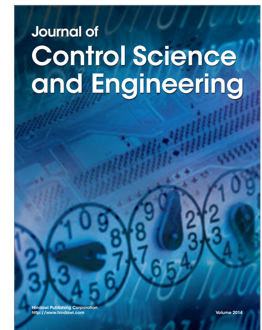
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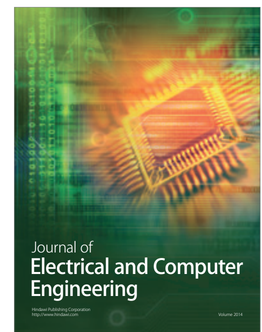
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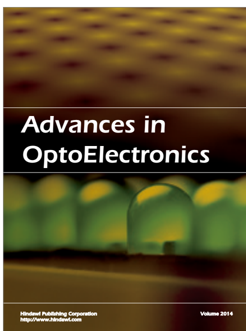
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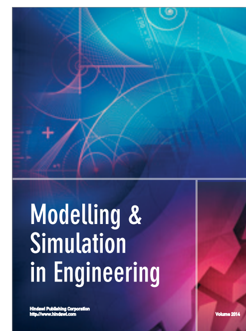
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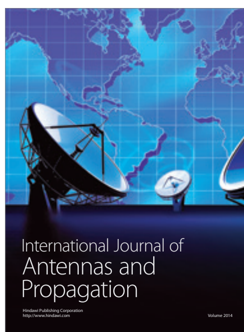
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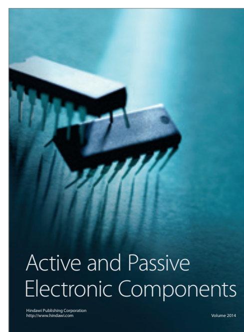
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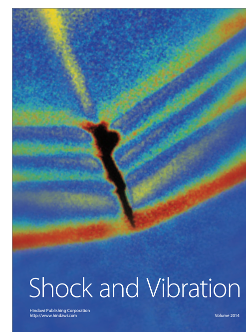
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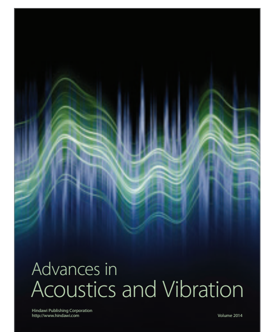
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