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Effect of doping concentration, solvent proportions and solution aging on the figure of merit of chemically sprayed ZnO:F thin films

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Abstract
Undoped zinc oxide (ZnO) and fluorine doped zinc oxide (ZnO:F) thin films were deposited on sodalime glass substrates by the ultrasonic chemical spray technique. The effect of the relevant deposition variables, namely, doping concentration, solvent proportions and solution aging on the Haacke´s Figure of Merit, φ_M, of ZnO:F thin films, is reported for the first time. φ_M was evaluated from the optical and electrical characteristics of the films. A wide range of F/Zn doping from 5 to 90 at%, in the starting solution, was used due to the high volatility of F during the deposition process and the concomitant poor incorporation into the ZnO lattice. In order to have F-doped solutions with high chemical stability, a mix of acetic acid:water:methanol, at different volume proportions, were tested as solvent; nevertheless the φ_M magnitudes remain unchanged, irrespective of solvent proportions. Regarding solution aging, despite it is a deposition variable that no plays any role in similar wide band gap semiconductor oxides, in the case of ZnO:F films, φ_M was significantly influenced through the electrical transport properties. Complementary information on structural and morphological characteristics of deposited ZnO:F thin films, for films with high φ_M, is also reported. From the results, optimization of deposition variables was achieved, as highly conductive and transparent ZnO:F thin films with a maximum, $\varphi_M = 7.57 \times 10^{-3}\ (\Omega/\square)^{-1}$, were deposited with a doping concentration of 30 at%, solvent proportion of 50:50:900, and an aging of 37 days. The obtained results show that ZnO:F thin films are potential candidates for transparent conductive oxide applications.

1 Introduction

Chemically sprayed (CS) fluorine-doped zinc oxide (ZnO:F) thin films, with low electrical resistivity and high optical transmittance in the visible region, present potential application in a wide variety of optical and optoelectronic devices [1–7]. In addition, the ZnO:F films have good thermal and chemical stability [8, 9]. The combination of chemical spray and the abundance of zinc favor the low price manufacturing of thin films for large scale applications. Hu and Gordon [10] stated the two main advantages of F doping as compared to In and Al doping of ZnO thin films; (1) the fluorine doping disturbs only the valence band and leaves the conduction band unaffected, so that the electron mobility remains high, and (2) the size of F and O ions is almost equal.

As a result, some interesting works, based on chemical spray deposition technique, regarding the effect of usual deposition variables on the characteristics of ZnO:F thin films has been reported [11–15]. However, despite the adequate characteristics and low cost manufacturing, CS ZnO:F has not attracted interest as occurs in the case of both CS Indium

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doped ZnO or Aluminum doped ZnO thin films. It is worthy to note that in the few reports on chemically sprayed ZnO:F, some differences are encountered, since different F concentrations in starting solution and deposition temperatures has been reported for optimum conditions [16]. Moreover, the aging time of the starting solution, that leads to highly conductive and transparent ZnO:F thin films, is a new variable found in the chemical spray technique that influences the electrical characteristics, a situation not usual in other semiconductor oxides thin films deposited by CS [17]. As a matter of fact, in the case of ZnO:In or ZnO:Al cases, the deposition is straightforward as no aging of solution is necessary for the deposition of conductive and transparent thin films [18]. In order to gain a better understanding about the effect of the solution aging on the chemical, more detailed work is needed. In this respect, the effect of precursors and solvents on similar systems can help to study CS ZnO:F thin films [19–24].

Regarding the possible location of F ions into the ZnO lattice, a few works regarding theoretical modeling of F doping have been published. Among them stands out the work of Liu et al. [25], where they have shown that starting from first principle calculations, under low oxygen condition, F can substitute O; further increase in F doping leads to F interstitial. However, due to the high activation energy formation, neither F in O sites nor F interstitial can provide electrons at room temperature. Then the decrease in electrical resistivity of ZnO:F thin films can be explained by the surface passivation of electrically active scattering sites on the grain boundaries by fluorine doping. A similar situation occurs with Al doped ZnO thin films [26], where it is also claimed that Al_2O_3 synthesis on the grain boundaries is favored during the formation process, due to the high chemical activity of Al ions that reacts with oxygen ions. In that case, the formation of Al_2O_3 clusters passivates all the traps present in the material. Authors conclude that substitution of Zn by "free" Al^{3+} ions into the ZnO lattice is unlikely to occur.

On the other hand, the determination of the F profile into the ZnO lattice is hard to obtain by conventional techniques based in electron beams, due to the high volatility of light ions during the interaction process [27, 28]. By the same reason it is also hard to determine the valence states of the fluorine compounds formed. It was not until reliable profile techniques based on nuclear reactions that F content could be determined in other systems [29].

As has been briefly outlined, in the processing of ZnO:F thin films by the chemical spray technique, there are still many issues to study in order to have a more complete knowledge of the factors affecting the transport properties. The possibility to reach the theoretical value for high electrical conductivity and transparency in the visible spectrum in ZnO:F thin films is far to reach yet, and more systematic and reliable experimental work is needed to reach this quest. The quality of a transparent conducting oxide, TCO, can be evaluated by means of the equilibrium between the sheet resistance (R_S) value and the average optical transmittance (T) at 550 nm that is the medium value in the visible region. The definition of Haacke´s Figure of Merit (ϕ_M) is now accepted as a judicious evaluation of optical transmittance, T, (measured at 550 nm) in percent and electrical sheet resistance, R_S, (measured in Ω/□) in semiconductor oxides for TCO applications that does not require more than 90% of optical transmittance [30], and it is defined by equation, $\phi_M = \frac{T^{10}}{R_S}$.

Fluorine doped ZnO films with high optical transmittance (~70%) and low sheet resistance (<400 Ω/□) leads to a Figure of Merit, which is promising for transparent electrodes.

In this work, the deposition of ZnO:F on sodalime glass substrates by the ultrasonic chemical spray is reported. The effect of F concentration in starting solution, the solvent proportions and the aging time of the starting solution on the electrical and optical characteristics were studied. We considered that Haacke´s Figure of Merit is an estimation for a fast feedback in the identification of optimum deposition conditions for manufacturing transparent electrodes. Structural and morphological properties of deposited ZnO:F films are presented as well.

2 Experimental procedure

ZnO:F thin films were deposited on sodalime glass substrates by the ultrasonic spray pyrolysis (USP) technique from 0.2 M starting solutions prepared with zinc acetate dissolved in a mix of deionized water, acetic acid and methanol in different volume proportion. The volume proportions were varied in order to study the effect on the electrical and optical characteristics of ZnO:F thin films, starting from a fresh solution. Maximum water content was 100 ml/l, as the commercial ultrasonic equipment has a limit for water content in the mix, and a further increase hinders the solution pulverization as the effective density increases. Table 1 shows the volume proportions of acetic acid, water and methanol, for the dissolution of zinc acetate. All films were deposited at 450 °C for 8 min.

Ammonium fluoride was selected as dopant. In this case, to facilitate the dopant addition, a 1.6 M NH_3F solution, dissolved in deionized water, was prepared. The doping was referred to the atomic ratio percent values, [F]/[F + Zn] at%; and the selected values were, 0, 5, 15, 30, 45, 60, 70 and 90 at%. Glass substrates with dimensions of 2.5 × 5 cm^2 were ultrasonically cleaned previously in an alkaline free-soap solution for 2 min, rinsed three times in deionized water and finally dried with a nitrogen jet. The deposition was carried out in a home-made equipment. Substrate temperature was

Table 1 Volume proportions, acetic acid:water:methanol, used for preparing the different starting solutions used in this work

Acetic acid (ml)	Water (ml)	Methanol (ml)
150	100	750
150	50	800
125	25	850
100	100	800
100	50	850
50	50	900
85	25	880
75	25	900

varied from 400 to 500 °C, in steps of 25 °C, whereas the deposition was kept at 8 min, respectively. The solution flow was adjusted to 1 ml/min for all depositions.

The aging of the starting solution was examined for an extended period of days in order to monitoring the variation in the sheet resistance of the ZnO:F thin films. The different solvent proportions used are reported in Table 2.

3 Results and discussion

3.1 Structure properties

The structure analysis of deposited ZnO:F thin films with different doping levels of F in the starting solution showed that the films were polycrystalline, fitting well with the hexagonal wurtzite structure [31]. Despite the high amount of F into the solution, no extra phases were encountered other than ZnO. This fact shows that F volatilization occurs, and only a small amount is incorporated into the films, below the solubility limit. Figure 1 shows the X ray diffraction spectra of ZnO:F thin films deposited with different F concentrations in the starting solutions. The peak associated to (002) planes prevails in all the spectra.

3.2 Electrical properties

The variation in the sheet resistance of ZnO:F thin films is shown in the Table 3 as a function of the F content in the starting solution. The sheet resistance reference value of ZnO:F films, for 0% F content, shows a high sheet resistance, in the order of 68 KΩ/□, for a film with a thickness of 340 nm. As the F content increases, the corresponding sheet resistances decrease, reaching a minimum value in the range of 420–320 Ω/□ for F concentration in solution in the range of 30–60 at%. Further increase in F content also increases the sheet resistance. It is worthy of mention that, despite of deposition time was constant, films thickness varied in every film, as consequence of variation of the rest of the deposition variables.

The best Figure of Merit, 8.4×10^{-5} $(\Omega/\square)^{-1}$, is still far from being adequate for applications as a transparent electrode. A possible reason of this result can be due to the fact of the high volatility of F, despite of the high concentrations contained in the fresh solution. Then, only a very small fraction of F is bounded in the lattice, affecting the transport properties significantly. Therefore, we consider that, it is necessary to link F to a heavy chain in order to improve the incorporation of F into ZnO structure.

In Fig. 2 it is shown the evolution of Figure of Merit, φ_M of ZnO:F thin films. As the F concentration increases in the solution, the φ_M increases, reaching a maximum value, 1.48×10^{-4} around an [F]/[F + Zn] doping concentration of 45 at%.

3.3 Morphological properties

Figure 3 shows the morphologies of ZnO:F thin films for two F concentrations, 60 and 90 at%, which are the two samples optimized in φ_M. For the case of ZnO:F deposited with a F concentration of 60 at% concentration in the solution, hexagonal shaped slices, with no screw defects on the top surface are formed with a wide size distribution. The average diameter of the flat slices ranges from 100 to 600 nm.

Table 2 Deposition conditions of ZnO:F thin films

Volume proportion of acetic acid:water:methanol	Doping concentration [F]/[F + Zn] (at%)	Substrate temperature (°C)	Deposition time (min)	Aging time (days)
150:100:850				5
150:50:800				15
125:25:850	30	450	8	30
100:100:800	45	475		90
100:50:850	60	500		100
50:50:900				
85:25:890				
75:25:900				

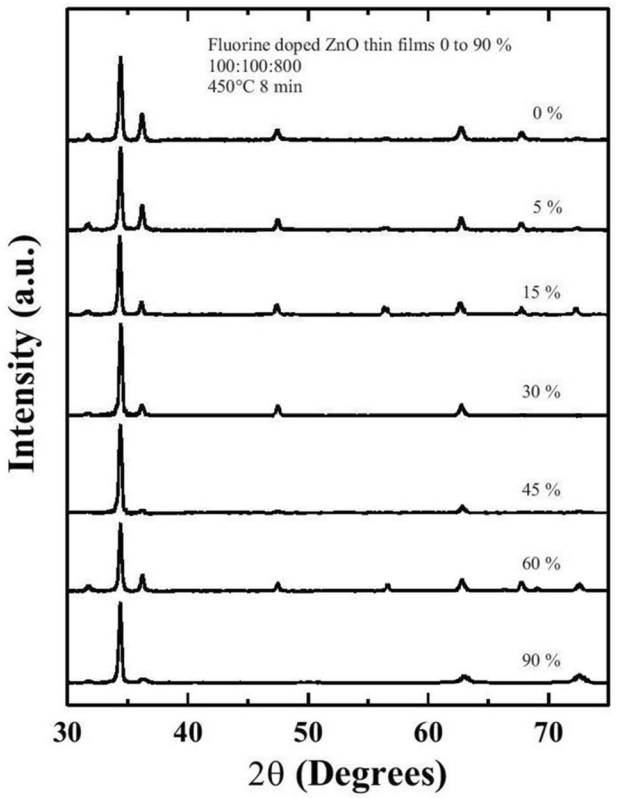

Fig. 1 X-ray diffraction patterns of ZnO:F films deposited with different F content

In Fig. 3b, the morphology of ZnO:F films doped with F concentration of 90% in starting solution shows the formation of hexagonal slices, although the average diameter is now restricted to 350 nm.

3.4 Solvent proportions effect

The effect of volume proportion of solvents on the characteristics of ZnO:F thin films were explored making systematic variations of volume proportions of acetic acid: water: alcohol. As previous results show that minimum electrical resistivity of films was found when F concentration ranged from 30 to 60 at%, a new exploration of this parameter was done again in this interval. The reference value, 0 at%, doping, was also included in this analysis step.

In the Table 4, it is shown the effect of the change in volume proportions of solvents on the optical transmittance estimated at 550 nm and the sheet resistance of ZnO:F thin films.

It can be seen that, the acetic acid:water:methanol volume proportion affects the transport properties of films, since a decrease in the sheet resistance was observed when water concentration decreases, but the acetic acid content is equal or higher than 100 ml. A decrease in acetic acid leads to an increase in the sheet resistance as can be seen in the Table 4. ZnO:F thin films with lowest sheet resistance were obtained for solution with a volume proportion of solvents of 100:100:800.

As the F content in the solution increases, the optical transmittance of ZnO:F films increases, when compared with no doped films. The fluorine doping combined with the variation in solvent proportions, increases the Figure of Merit of ZnO:F films, from 10^{-7} to 10^{-5} $(\Omega/\square)^{-1}$.

3.5 Solution aging effect and figure of merit

Table 5 shows the effect of the aging of solution and the substrate temperature on the electrical and optical characteristics of ZnO:F thin films. Complementary exploration was made with the solvent proportions and deposition time of the films. Solution aging affects dramatically the electrical resistance of ZnO:F thin films, as sheet resistance values below 100 Ω/□ are now easily obtained. The ZnO:F films are competitive with those doped with In or Al, which makes adequate as transparent electrodes. The Figure of Merit is also enhanced, as high values in the order of 7.5×10^{-3} $(\Omega/\square)^{-1}$ were also obtained. The doped films deposited from aged solutions show mirror like finish at naked eye, which was confirmed with optical transmittance measurements.

Table 3 Figure of Merit values of ZnO:F thin films deposited at 450 °C and 8 min, from starting solutions with different F concentrations, volume proportion of solvents 100:100:800

Doping concentration [F]/[F + Zn] at%	Optical transmittance T (%)	Sheet resistance R_S $(\Omega/\square)\times10^3$	Thickness film (nm)	Figure of merit $\phi_M(\Omega/\square)^{-1}$
0	60	68	343	1.04×10^{-7}
5	62	5.3	369	1.64×10^{-6}
15	73	3.5	347	1.23×10^{-5}
30	66	0.4	441	3.75×10^{-5}
45	81	0.8	234	1.48×10^{-4}
60	69	0.3	438	8.40×10^{-5}
70	78	1	265	8.69×10^{-5}
90	89	2.3	261	1.45×10^{-4}

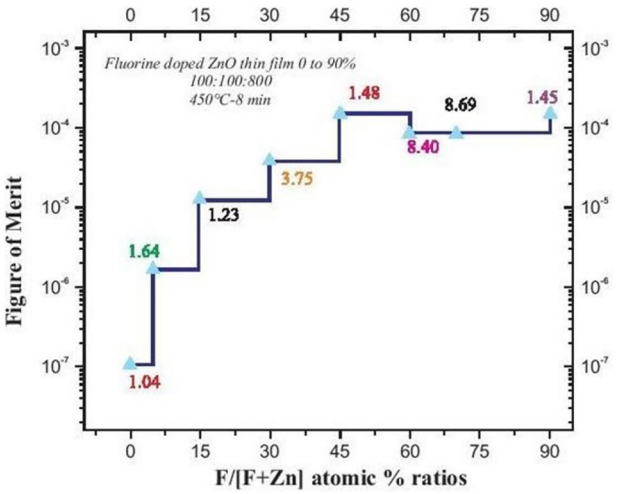

Fig. 2 Effect of fluorine content on the Figure of Merit, $\varphi_{M,}$ of ZnO:F thin films

Summarizing the results, the influence of F concentration in the starting solution, the variation of solvent proportions and the aging of the solution on electrical and optical characteristics of ZnO:F thin films deposited by the ultrasonic spray pyrolysis technique can be observed in the Table 5. From the values reported, it is observed that, for fresh solutions, as the F concentration was increased, a decrease in the sheet resistance of ZnO:F thin films was obtained. The F concentration, ranging from 30 to 60 at%, was the interval where sheet resistance decreases. The minimum value of sheet resistance was in the order of 230 Ω/□. Comparing this value with the minimum obtained in ZnO:F thin films deposited with pneumatic spray pyrolysis technique, in the order of 500 Ω/□ [32], it is seen that ultrasonic deposition enhances the transport properties with fresh solutions. This result can be due to the fact that, ultrasonic pulverization generates drops with a smaller diameter, and the deposition process resembles a CVD process. The exploration of the effect of solvent proportions in films deposited with fresh solutions, shows that no significant enhancement occurs in the electrical properties.

The effect of the aging of the solution on the characteristics of ZnO:F films shows the relevance of chemical species for an effective doping. Unfortunately, the diamagnetic character of Zn hinders the application of techniques to track the evolution of chemical species as a function of the time. Based in pH indicators, it has been observed that, as the time increases, the values measured in the solution tend to increase from 4.2 to 5.1. Aging process of solution leads to films highly conductive and transparent, as sheet resistances in the order of 27 Ω/□ and 85% of optical transmittance were obtained.

Once it has been established that solution aging enhances transport properties, it arises the need for reducing cost in film manufacturing. In principle, solution aging process can be catalyzed shortening the time solution is ready for deposition of conductive films. This goal can be reached either with additives in the solution or modifying the precursors. In order to continue this work, it remains the study of the effect of Zn and F precursors on the characteristics of ZnO:F films under similar conditions. This work is in due course.

4 Conclusions

Conductive and transparent ZnO:F thin films were successfully deposited on sodocalcic glass with the ultrasonic spray pyrolysis technique. The solution composition and the substrate temperature play a major role on the characteristics of ZnO:F films. In the case of fresh solutions, the Figure of Merit is very low. The CVD character of the deposition process of ZnO:F films, in the case of ultrasonic atomization, overpass pneumatic synthesis, as films with a

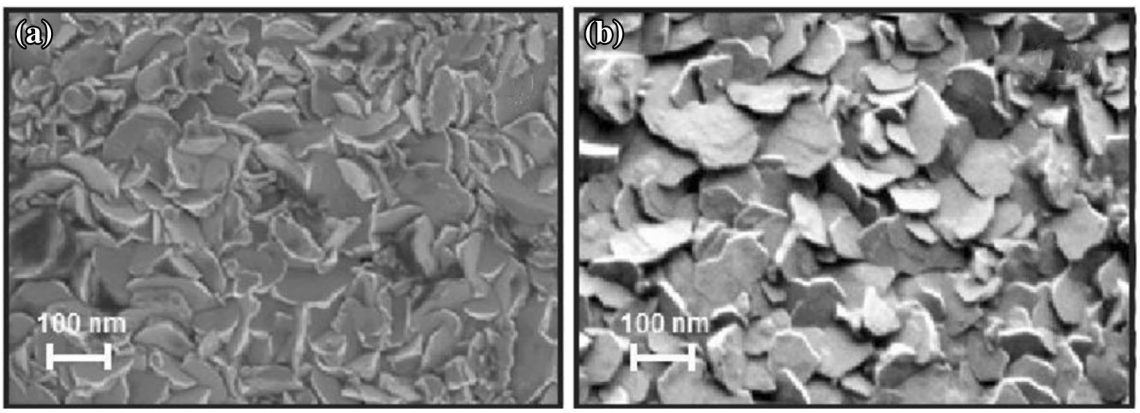

Fig. 3 SEM micrographs of ZnO:F thin films deposited at two different F concentration and 450 °C: **a** 60 at%, and **b** 90 at%

Table 4 Optical, electrical and Figure of Merit of ZnO:F thin films deposited with different solutions and solvent proportions and at 450°C

Volume proportion of acetic acid: water: methanol	[F]/[F+Zn] at%	Optical transmittance (%)	$R_S \times 10^3$ (Ω/□)	Thickness (nm)	$\varphi_M(\Omega/\square^{-1})$
150: 100: 750	0	52.91	44.26	348	3.88×10^{-7}
	30	62.55	17.40	391	5.26×10^{-6}
	45	69.71	37.60	321	7.20×10^{-6}
	60	74.48	8.41	416	6.24×10^{-6}
150: 50: 800	0	79.8	86.20	268	1.21×10^{-6}
	30	60.31	1.20	462	5.30×10^{-6}
	45	74.90	0.98	473	5.67×10^{-5}
	60	74.14	0.77	489	6.5×10^{-5}
125: 25: 850	0	72.47	22.71	241	1.76×10^{-6}
	30	78.35	5.65	375	1.54×10^{-5}
	45	73.34	6.73	354	6.68×10^{-6}
	60	80.05	4.35	419	2.46×10^{-5}
100: 100: 800	0	60.99	68.20	343	1.04×10^{-7}
	30	66.16	0.427	441	3.75×10^{-5}
	45	81.26	1.07	234	1.24×10^{-4}
	60	69.68	0.321	438	8.40×10^{-5}
100: 50 :850	0	65.46	41.00	427	3.52×10^{-7}
	30	65.43	1.36	302	1.05×10^{-5}
	45	73.51	0.86	285	5.35×10^{-5}
	60	75.54	1.18	396	5.12×10^{-5}
50: 50 :900	0	69.5	73.00	301	3.6×10^{-7}
	30	79.69	2.16	239	4.78×10^{-5}
	45	80.54	4.6	211	2.4×10^{-5}
	60	93.35	8.42	265	5.96×10^{-5}
85: 25 :890	0	91.1	50.6	383	7.7×10^{-6}
	30	77.92	7.61	282	1.08×10^{-5}
	45	68.45	2.49	492	9.0×10^{-6}
	60	69.17	11.37	356	1.98×10^{-6}
75: 25 :900	0	71.26	89.00	277	3.79×10^{-7}
	30	83.48	18.10	264	9.08×10^{-6}
	45	74.49	3.27	415	1.6×10^{-5}
	60	79.53	11.50	322	8.80×10^{-6}

lower sheet resistance were deposited. Through the aging of the solution, chemical species formed facilitate incorporation of F into the ZnO lattice. The sheet resistance of films shows an enhancement when films were deposited with aged solutions. Optical transmittance of the films was not affected in a significant way by F doping when a fresh solution is used for depositing the ZnO:F thin films. Solution aging is a new variable in the chemical spray technique, opening new ways for sample preparation with enhanced characteristics.

Table 5 Film thickness, optical transmission, electrical sheet resistance, and figure of merit of ZnO:F thin films for different solution conditions at 450 C

Volume proportion of acetic acid:water:methanol	[F]/[F + Zn] (%)	Optical transmittance (%)	Sheet resistance ($\Omega/\square$)×10^3	Film thickness (nm)	Figure of merit, $\phi_M(\Omega/\square^{-1})$
150: 100: 750	0	52	44	348	3.88×10^{-7}
	30	62	17	391	5.26×10^{-6}
	45	69	37	321	7.20×10^{-6}
	60	74	8	416	6.24×10^{-6}
150: 50: 800	0	79	86	268	1.21×10^{-6}
	30	60	1.2	462	5.30×10^{-6}
	45	74	0.9	473	5.67×10^{-5}
	60	74	0.7	489	6.5×10^{-5}
125: 25: 850	0	72	22	241	1.759×10^{-6}
	30	78	5	375	1.54×10^{-5}
	45	73	6	354	6.68×10^{-6}
	60	80	4	419	2.46×10^{-5}
100: 100: 800	0	60	68	343	1.04×10^{-7}
	30	66	0.4	441	3.75×10^{-5}
	45	81	1	234	1.24×10^{-4}
	60	69	0.3	438	8.40×10^{-5}
100: 50 :850	0	65	41	427	3.52×10^{-7}
	30	65	1	302	1.05×10^{-5}
	45	73	0.8	285	5.35×10^{-5}
	60	75	1	396	5.12×10^{-5}
50: 50 :900	0	69	73	301	3.6×10^{-7}
	30	79	2	239	4.78×10^{-5}
	45	80	4	211	2.4×10^{-5}
	60	93	8	265	5.96×10^{-5}
85: 25 :890	0	91	50	383	7.7×10^{-6}
	30	77	7	282	1.08×10^{-5}
	45	68	2	492	9.0×10^{-6}
	60	69	11	356	1.98×10^{-6}
75: 25 :900	0	71	89	277	3.79×10^{-7}
	30	83	18	264	9.08×10^{-6}
	45	74	3	415	$1.6x10^{-5}$
	60	79	11	322	8.80×10^{-6}

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