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# Two-functional DC sputtered Cu-containing $TiO_2$ thin films

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ABSTRACT

The article reports on structure, optical properties, UV-induced hydrophilicity and biocidal activity of DC sputtered Cu-containing $TiO_2$ thin films. The $TiO_2$/Cu films with low (≤10 at.%) Cu content were reactively sputtered from a composed Ti/Cu target in a mixture of Ar + $O_2$ at different partial pressures of oxygen $p_{O_2}$ on glass substrates held on floating potential $U_{fl}$. This way $TiO_2$/Cu films with Cu homogeneously distributed in the whole volume of film were prepared. The main attention was concentrated on the effect of the amount of Cu added to $TiO_2$ film on its crystallization, structure, optical properties and correlations between the structure and (i) the hydrophilicity and (ii) the efficiency of killing of *Escherichia coli* bacteria on the surface of $TiO_2$/Cu composite film after UV irradiation. It is shown that ∼1000 nm thick $TiO_2$/Cu composite film with ∼1.5 at.% Cu exhibits simultaneously two functions: (1) good hydrophilicity with water droplet contact angle (WDCA) $\alpha \leq 20^{\circ}$ and (2) strong killing power for *E. coli*.



## 1. Introduction

Nowadays, great attention is devoted to the antibacterial activity of surfaces based on $TiO_2$ films containing different elements, such as Ag, Cu, Fe, etc. [1–18]. Highly reactive radicals, mainly $^{\bullet}OH$, or $O_2^-$ and $H_2O_2$, created during UV irradiation of $TiO_2$ films at first disrupt the outer lipid membrane of bacteria cell which is the main step in killing of bacteria [1,2]. It means that a sufficient amount of reactive radicals is needed. The $TiO_2$ surfaces containing low amount (of about several at.% or less) of the selected element exhibit improved UV-induced antibacterial activity. These composite films are denoted as $TiO_2$/Me. The surface of $TiO_2$/Me film exhibits not only a higher killing efficiency of bacteria but also makes it possible to remove the killed bacteria from the film surface due to excellent surface hydrophilicity induced by UV irradiation. Therefore, the $TiO_2$/Me composites are two-functional films. They exhibit simultaneously two UV-induced functions: (1) biocidal activity and (2) easy surface cleaning.

Metals such as Ag [3–10], Cu [11–14] or Fe [15–16] have been used in the $TiO_2$/Me antibacterial composite thin films. Such $TiO_2$/Me films are intoxicant if low amounts of these elements are incorporated into $TiO_2$ material. The addition of metal into $TiO_2$ results in (i) the reduction of surface recombination of photogenerated electrons and holes by trapping of photogenerated electrons with positive metal ions $Me^+$ and (ii) the enhanced creation of $^{\bullet}OH$ radicals, which very efficiently kill bacteria, by positive holes. Besides, the metal ions kill bacteria directly. For example, the $Cu^+$ ions penetrate through the outer cell wall and damage cytoplasmic membrane of bacteria cells [11]. These are main reasons for an enhancement of the killing of bacteria by incorporation of selected elements into $TiO_2$ thin films.

Pure $TiO_2$ film or $TiO_2$/Me composite films containing selected metallic elements Me are very often prepared by a sol–gel method [1,2]. However, such films exhibit low mechanical properties (hardness, wear, adhesion) and require high calcination temperatures to be used after deposition to achieve good hydrophilic and antibacterial properties. On the contrary, the magnetron sputtering is very convenient method for the preparation of dense, mechanically durable and well adherent films even at relatively low substrate temperatures $T_s \leq 200\,^{\circ}C$ [19–21]. However, at present a insufficient information on the biocidal activity of $TiO_2$/Me composite films are available. The effect of Me content in $TiO_2$/Me composite film on its structure and speed of UV-induced killing of bacteria need to be investigated in detail. The effective sterilization of bacteria is defined as the decrease of bacteria population by six orders of magnitude. This decrease is required to be achieved in very short time of several minutes.

The subject of this article is a systematic investigation of magnetron sputtered $TiO_2$/Cu composite thin films with the aim to investigate (i) the effect of Cu addition on the structure of film and its UV-induced surface hydrophilicity and antibacterial properties and (ii) to find deposition conditions under which the surface of

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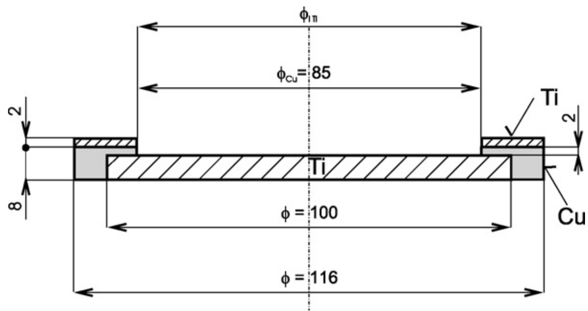


**Fig. 1.** Geometry and dimensions of composed Ti/Cu target.

the $TiO_2$/Cu film exhibits simultaneously good hydrophilicity and rapid killing (in several minutes) of *Escherichia coli*.

## 2. Experimental

The $TiO_2$/Cu films were reactively sputtered using an unbalanced magnetron equipped with a composed target (Ti round plate of diameter 100 mm with copper ring of inner diameter $Ø_{iCu}$ = 85 mm covered with Ti ring of inner diameter $Ø_{iTi}$, see Fig. 1) in Ar + $O_2$ mixture at the total pressure $p_T = p_{Ar} + p_{O_2} = 0.9$ and 2 Pa. The amount of Cu content in the $TiO_2$ film was controlled by the inner diameter $Ø_{iTi}$ of a top Ti ring. The $TiO_2$/Cu films were deposited in a cylindrical aluminum chamber (Ø = 150 mm, $L$ = 225 mm), pumped down to a base pressure $p_0 \approx 10^{-3}$ Pa, on glass substrates (26 × 26 × 1 mm$^3$) held on floating potential $U_{fl}$ and fixed to a substrate holder located in the substrate-to-target distance $d_{s\text{-}t}$ = 100 mm.

The $TiO_2$/Cu films were sputtered at: constant magnetron discharge current $I_d$ = 3 A, two values of substrate temperature $T_S$ = room temperature RT (unheated) and 500 °C and different values of partial pressure of oxygen $p_{O_2}$. The typical thickness h of $TiO_2$/Cu films was ∼1000 nm. The post-deposition thermal annealing of the $TiO_2$/Cu films was carried out in the deposition chamber on the substrate holder heated from RT up to the temperature $T_a$ = 500 °C with heating rate 16.6 °C/min and cooling rate 8.3 °C/min. The annealing at a given value of $T_a$ was performed for $t_a$ = 60 min. The thermal annealing was carried out in (i) vacuum at base pressure $p_0$ = 1 × 10$^{-3}$ Pa and (ii) oxygen at pressure $p_{O_2} = 10$ Pa.

The thickness of the films was measured by a stylus profilometer (DEKTAK 8) with a resolution of 0.1 nm. The structure of the films was characterized by X-ray diffraction using PANalytical X Pert PRO diffractometer in the Bragg-Brentano configuration with CuKα irradiation (λ = 0.154187 nm). The hydrophilicity of the surface of the $TiO_2$/Cu films was characterized by the water droplet contact angle (WDCA) α after its irradiation by the UV light (Philips TL-DK 30W/05, $W_{ir}$ = 0.9 W/cm$^2$, λ = 365 nm) using a Surface Energy Evaluation System (Masaryk University in Brno, Czech Republic). The optical transparency and the energy bandgap $E_g$ of the $TiO_2$/Cu films were evaluated from spectra measured by the spectrometer Specord M400 (Carl Zeiss Jena, Germany). The antibacterial activity of the $TiO_2$/Cu films was tested on killing of *E. coli* bacteria at the Department of Microbiology, Medical Faculty in Plzen of Charles University in Praha. The suspension of physiological solution (NaCl and distilled water) and bacteria *E. coli* was prepared with the concentration of bacteria 10$^6$ CFU/ml. The tribe of bacteria was selected coincidentally. 100 μl of suspension was applied on the surface of $TiO_2$/Cu film. Then, the sample placed in a box covered by a transparent plastic plate was irradiated by UV light for different times. The influence of the plastic plate on UV irradiation of sample was negligible. The temperature inside covered box during UV irradiation was 33 °C. After UV irradiation the suspension covered the surface of sample was washed down by 5 ml of physiological solution. From this new solution a 10 μl was abstracted and spread on the Petri dish with Endo agar. The agar with spread suspension was cultivated 24 h in a biological thermostat at constant temperature 37 °C. The grown *E. coli* colonies were clearly visible and counted.

## 3. Results and discussion

### 3.1. Crystallization of $TiO_2$/Cu film containing 4.6 at.% Cu

It is well known that crystallization of the film depends on the energy $E$ delivered to it during growth by (i) the substrate heating, (ii) bombarding ions and condensing atoms, and (iii) post-deposition thermal annealing.

At first, the effect of $T_s$ and $p_T$ on the structure of as-deposited $TiO_2$/Cu film was studied. The evolution of the structure of $TiO_2$/4.6 at.% Cu film, sputtered from a composed target with Ti ring of inner diameter $Ø_{iTi}$ = 85 mm at two values of $p_T$ = 0.9 and 2 Pa and $T_s$ increasing from the room temperature (RT) to 500 °C, is displayed in Fig. 2. All films were sputtered in the oxide mode at the same values of (i) the deposition time $t_d$ = 100 min and (ii) the film deposition rate $a_D \approx 10$ nm/min. This experiment shows that:

1. The total pressure $p_T$ of sputtering gas mixture has a stronger effect on the crystallization of $TiO_2$ films than the substrate temperature $T_s$.
2. The total pressure $p_T \leq 0.9$ Pa is sufficient to form crystalline $TiO_2$ films on unheated glass substrates.
3. The rutile phase dominates over the anatase one in the case when the partial pressure of oxygen $p_{O_2} < p_c$ because an insuf-

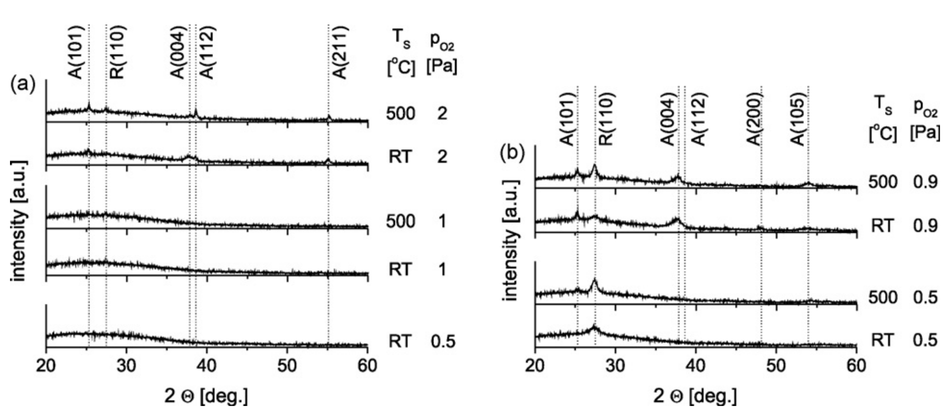


**Fig. 2.** Structure of ∼1000 nm thick $TiO_2$/Cu films with 4.6 at.% Cu sputtered at $I_d$ = 3 A, $U_s = U_{fl}$ and $a_D \approx 10$ nm/min on glass substrate for different values of $T_s$, $p_{O_2}$ and $p_T$ = 2 Pa (a) and $p_T$ = 0.9 Pa (b) and characterized with XRD patterns.

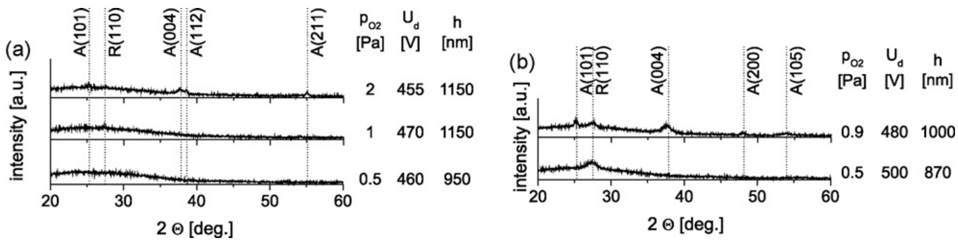


**Fig. 3.** Evolution of structure of ~1000 nm thick $TiO_2$/Cu films with 4.6 at.% Cu, sputtered with $a_D \approx 10$ nm/min on unheated ($T_s$ = RT) glass substrate at $I_d$ = 3 A, $U_s = U_{fl}$ and $p_T$ = 2 Pa (a) and $p_T$ = 0.9 Pa (b), with increasing $p_{O_2}$.

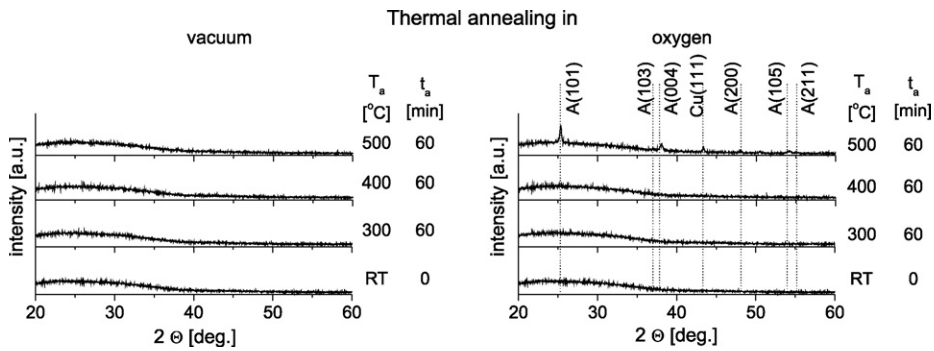


**Fig. 4.** Effect of thermal annealing in vacuum ($1 \times 10^{-3}$ Pa) and oxygen (10 Pa) for 60 min on crystallization of amorphous $TiO_2$/Cu film with 4.6 at.% Cu. As-deposited $TiO_2$/Cu film was sputtered at $I_d$ = 3 A, $U_s = U_{fl}$, $p_{O_2} = 0.5$ Pa, $p_T$ = 2 Pa on unheated substrate.

ficient amount of oxygen atoms is available for the creation of the stoichiometric $TiO_{x=2}$ oxide; $p_c$ is the partial pressure of oxygen which enable to generate such amount of O atoms which is necessary to form the stoichiometric $TiO_{x=2}$ oxide. The value $p_c$ depends on the film deposition conditions, particularly $I_d$, $U_d$, $U_s$ and $d_{s\text{-}t}$, and the substrate temperature $T_s$; here $U_d$ and $U_s$ is the discharge voltage and the substrate bias, respectively. For more details on formation of the anatase phase see the references [19–20].

The last conclusion is confirmed also by the experiment in which the effect of $p_{O_2}$ on the structure of $TiO_2$/4.6 at.% Cu film sputtered on unheated glass substrates was investigated, see Fig. 3. From this figure it is seen that the increase in $p_{O_2}$ from 0.5 to 2 Pa improves the formation of the anatase phase in $TiO_2$/4.6 at.% Cu film but only in the case if sputtered at high value of $p_T$ = 2 Pa where sufficient amount of O atoms to form stoichiometric $TiO_{x=2}$ oxide is available.

The experiments results which are displayed in Figs. 2 and 3 show that the formation of $TiO_2$ film with a dominant anatase phase require high $p_{O_2}$ and high $T_s$ to be used. Such a combination of $p_{O_2}$ and $T_s$ is necessary due to a low ionization degree of sputtering gas mixture even in the discharges of the best magnetrons currently used. As soon as new advanced magnetrons with a higher ionization of reactive gas will be developed, it will be possible to decrease $p_{O_2}$ and $T_s$ and to create the $TiO_2$ films with the dominated anatase phase at lower values of $T_s$, maybe also at RT. It is a great challenge for the development of new magnetrons.

### 3.2. Thermal annealing of $TiO_2$/Cu film with low (<5 at.%) and high (>5 at.%) Cu content

Two experiments with the aim to investigate the effect of a post-deposition thermal annealing on the crystallization of $TiO_2$/Cu films were performed. In the first experiment the X-ray amorphous 1000 nm thick a-$TiO_2$/Cu film with 4.6 at.% of Cu content, sputtered at $I_{da}$ = 3 A, $p_{O_2} = 0.5$ Pa and $p_T$ = 2 Pa, was thermally annealed in vacuum ($1 \times 10^{-3}$ Pa) and in oxygen (10 Pa), see Fig. 4. In the second experiment the thermal annealing in oxygen (10 Pa) of two as-deposited a-$TiO_2$/Cu films with different Cu content was investigated, see Fig. 5. The aim of the second experiment was to find how the Cu content in $TiO_2$/Cu film influences its crystallization during the thermal annealing in oxygen.

From XRD patterns displayed in Figs. 4 and 5 the following conclusions can be drawn. Thermal annealing in both the vacuum and the oxygen at $T_a$ < 500 °C for 60 min is insufficient to stimulate the crystallization of a-$TiO_2$/Cu film with 4.6 at.% Cu. a-$TiO_2$/Cu

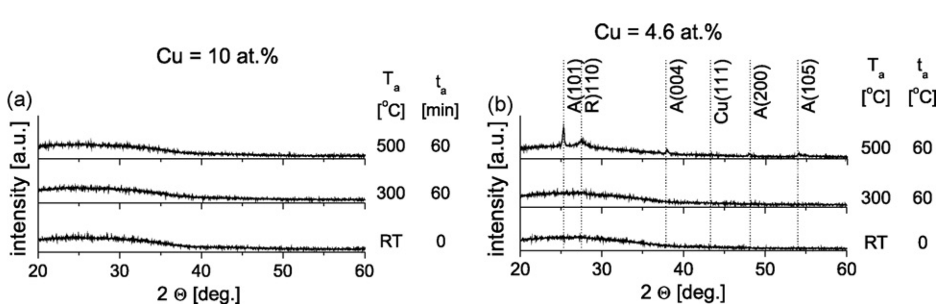


**Fig. 5.** Change of structure of 1000 nm thick $TiO_2$/Cu films with (a) high (10 at.%) and (b) low (4.6 at.%) Cu content sputtered at $I_d$ = 3 A, $p_{O_2} = 0.5$ Pa and $p_T$ = 2 Pa after annealing at temperatures $T_a$ = 300 and 500 °C in oxygen at pressure 10 Pa.

**Table 1**
Effect of the post-deposition thermal annealing of 1000 nm thick a-$TiO_2$/Cu film with 4.6 at.% Cu in vacuum and oxygen at different annealing temperatures $T_a$ for 60 min on its transmittance $T$ at $\lambda$ = 550 nm and optical band gap $E_g$. Deposition conditions of a-$TiO_2$/4.6 at.% Cu film: $I_d$ = 3 A, $U_s = U_{fl}$, $p_{O_2} = 0.5$ Pa, $p_T$ = 2 Pa, unheated glass substrate.

| $T_a$ [°C] | Thermal annealing in | | | | | |
|---|---|---|---|---|---|---|
| | Vacuum ($1 \times 10^{-3}$ Pa) | | | Oxygen (10 Pa) | | |
| | $T$ [%] | $E_g$ [eV] | Structure | $T$ [%] | $E_g$ [eV] | Structure |
| None | 74 | 2.84 | a- | 74 | 2.84 | a- |
| 300 | 40 | 2.34 | a- | 43 | 2.45 | a- |
| 400 | 29 | 1.61 | a- | 20 | 1.40 | a- |
| 500 | 27 | 1.42 | a- | 50 | 3.13 | nc- |

a-, X-ray amorphous structure; nc-, nanocrystalline structure.

film with low (4.6 at.%) Cu content crystallizes during annealing in oxygen at $T_a$ = 500 °C for 60 min. Thermal annealing in oxygen at $T_a \le 500$ °C for 60 min is insufficient to stimulate the crystallization of a-$TiO_2$/Cu film with high (10 at.%) content of Cu.

These results indicate that for the crystallization of a-$TiO_2$/Cu film the partial pressure of oxygen $p_{O_2} \ge 0.5$ and the thermal annealing at $T_a \ge 500$ °C for 60 min or more are needed. Moreover, it is worthwhile to note that the thermal annealing of a-$TiO_2$/Cu film induces strong changes of its properties in spite of the fact that the $TiO_2$/Cu film after annealing remains X-ray amorphous. The transmittance $T$ at $\lambda$ = 550 nm and the optical band gap $E_g$ decrease with increasing $T_a$, see Table 1. It indicates that observed changes in the film properties are a result of changes of the film nanostructure induced during thermal annealing. Changes of the film structure from X-ray amorphous to nanocrystalline one induced by selection of deposition parameters ($p_T$, $p_{O_2}$, $T_s$, $I_d$, $U_d$) and or parameters of the post-deposition thermal annealing ($T_a$, $t_a$) are of key importance for the understanding of the process of a nanocrystallization from amorphous phase. These changes are now investigated in our labs. Fig. 4 clearly shows that the nanocrystallization can be achieved at lower $T_a$ if the thermal annealing is performed in oxygen in comparison with annealing in vacuum. The XRD pattern of nc-$TiO_2$/Cu film are composed of low-intensity X-ray reflections from $TiO_2$ nanograins with anatase structure and Cu nanograins both superposed on an X-ray amorphous "hallo" from a-$TiO_2$ phase. It indicates that the nc-$TiO_2$/Cu film is composed of anatase $TiO_2$ and Cu nanograins embedded in a-$TiO_2$ matrix. The occurrence of low-intensity X-ray reflections is accompanied by a jump increase of the optical transmittance $T$ and the optical band gap $E_g$ of the $TiO_2$/Cu film.

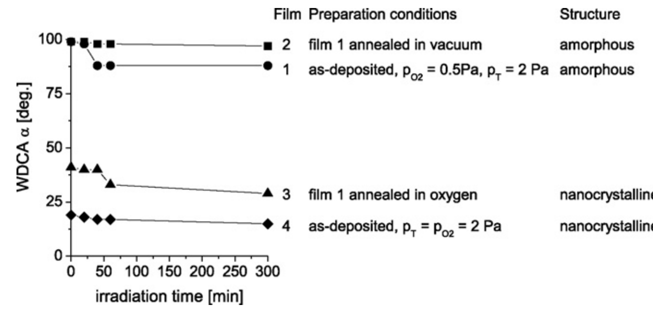


**Fig. 6.** WDCA $\alpha$ of $TiO_2$/Cu film with 4.6 at.% Cu: (a) as-deposited amorphous $TiO_2$/Cu film (film 1), (b) amorphous $TiO_2$/Cu film annealed in vacuum (film 2), (c) amorphous $TiO_2$/Cu film annealed in oxygen (film 3) and (d) as-deposited nanocrystalline $TiO_2$/Cu film (film 4). Thermal annealing was performed at $T_a$ = 500 °C for 60 min.

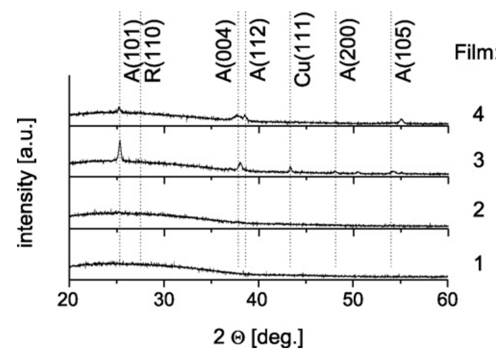


**Fig. 7.** XRD patterns from $TiO_2$/Cu films denoted as the films 1, 2, 3, and 4 and used in investigation of its WDCA $\alpha$ the values of which are displayed in Fig. 6.

## 3.3. Hydrophilicity of $TiO_2$/Cu films

The hydrophilicity of $TiO_2$/Cu film is stimulated by the UV light irradiation and is characterized by a water droplet contact angle (WDCA) $\alpha$. $\alpha$ is measured after a given time $t_{UV}$ of UV irradiation and is denoted as $\alpha_{tUV}$, e.g. $\alpha_{60UV}$ denotes the $\alpha$ after 60 min of UV irradiation. The $\alpha$ strongly depends on the structure of as-deposited $TiO_2$/Cu films and on the time of its post-deposition thermal annealing, see Fig. 6. The XRD patterns from four $TiO_2$/Cu films deposited on unheated glass substrate, denoted as a films 1, 2, 3 and 4, are given in Fig. 7.

The amorphous films are hydrophobic and exhibit high $\alpha \approx 90$–100°. The thermal annealing of the as-deposited amorphous $TiO_2$/Cu film at $T_a$ = 500 °C for 60 min is insufficient for its crys-

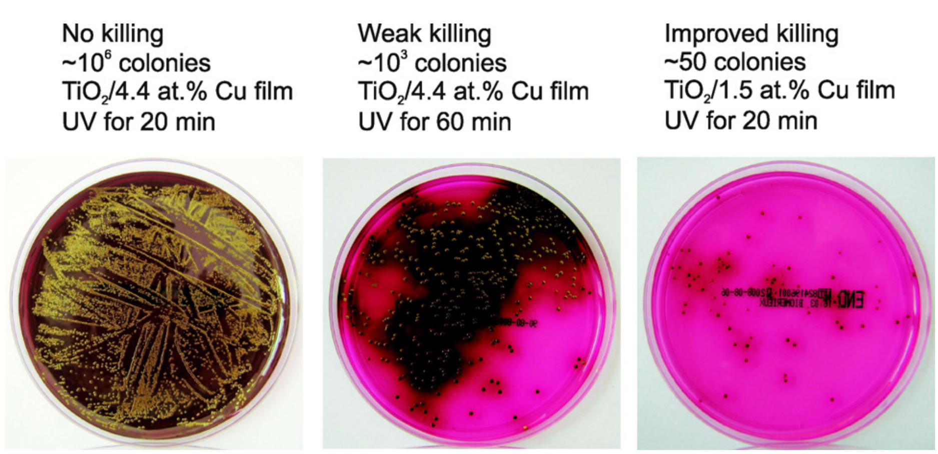


**Fig. 8.** Photos illustrating the efficiency of killing of *E. coli* bacteria grown on Endo agar covering surface of Petri dish after preceding exposure to UV irradiation on surface of $TiO_2$/Cu film with different content of Cu and next cultivation for 24 h at 37 °C.

tallization and even results in the increase of $\alpha$ (up to $\sim$100°). The as-deposited nanocrystalline $TiO_2$/Cu film exhibits much better surface hydrophilicity with $\alpha \approx 20°$ even without the UV irradiation. The UV irradiation of this film results in very negligible decrease of $\alpha$; $\alpha$ decreases only by 5° from 20° to 15° after 300 min of UV irradiation. The origin of this phenomenon is unclear and needs further investigation, which is, however, out of the scope of this paper.

### 3.4. Photokilling of bacteria on $TiO_2$/Cu thin films

The biocidal activity of $TiO_2$/Cu films was tested by killing of the bacterium *E. coli* on the surface of the $TiO_2$/Cu single layer film sputtered on unheated glass substrate during UV irradiation for a given time $t_{ir}$. Obtained results are shown in Figs. 8. Fig. 8 shows photos of (a) the Petri dish covered with Endo agar and *E. coli* colonies after UV irradiation on the $TiO_2$/4.4 at.% Cu film for 20 and 60 min and the $TiO_2$/1.5 at.% Cu film and next cultivation for 24 h at 37 °C. The initial concentration of bacteria prior to UV irradiation was $10^6$ CFU/ml; here 1 CFU = 1 bacterium. The following results were obtained:

1. No killing of bacteria after 20 min of UV irradiation on the surface of $TiO_2$/4.4 at.% Cu film is seen in Fig. 8a (the round spot = 1 bacteria colony created by 1 CFU).
2. Weak killing of bacteria after 60 min of UV irradiation on the surface of $TiO_2$/4.4 at.% Cu film is seen in Fig. 8b ($\sim10^3$ CFU).
3. Enhanced killing of bacteria after 20 min of UV irradiation on surface of $TiO_2$/1.5 at.% Cu film is seen in Fig. 8c ($\sim$50 CFU).

These experiments show that the efficiency of the killing of bacteria depends not only on the time $t_{ir}$ of the UV irradiation but very strongly also on the content of Cu in the $TiO_2$ films. The $TiO_2$/1.5 at.% Cu film exhibits the better results. Therefore, a biocidal activity of the $TiO_2$/1.5 at.% Cu film was investigated in more detail. The $TiO_2$/1.5 at.% Cu films were prepared at different values of the partial pressure of oxygen $p_{O_2}$. Then, the efficiency of killing of the *E. coli* bacteria on the surface of these films during UV irradiation for 20 and 30 min were tested. It was found that the efficiency of $TiO_2$/1.5 at.% Cu films improves with increasing $p_{O_2}$.

As expected, this experiment shows that the biocidal activity of $TiO_2$/Cu film depends not only on the content of Cu but also on structure of $TiO_2$ films. The increase of $p_{O_2}$ improves not only the crystallinity of $TiO_2$/Cu film but also results in the suppression of formation of the rutile phase on expense of the growth of anatase phase. The dominance of the anatase phase in the $TiO_2$/Cu film seems to be the main reason for the improvement of the biocidal activity of the $TiO_2$ film alloyed with Cu. The key result of this experiment is the finding that $TiO_2$ films with anatase structure containing 1.5 at.% Cu are two-functional films which exhibit simultaneously a good UV-induced hydrophilicity and best biocidal activity.

## 4. Conclusions

Main results of our investigation can be summarized as follows:

1. The crystallization of $TiO_2$/Cu thin films can be induced either by increasing of the substrate temperature $T_s$ during sputtering (one-step process) or by a post-deposition thermal annealing (two-step process).
2. The alloying of $TiO_2$ thin films with Cu and variation of substrate temperature $T_s$ strongly influences their structure. The $TiO_2$/Cu films with high ($\geq$10 at.%) Cu content reactively sputtered on the glass substrate held on a floating potential $U_s = U_{fl}$ at $T_s \leq 500$ °C are X-ray amorphous. On the contrary, $TiO_2$/Cu films with low (<10 at.%) Cu content are well crystallized when sputtered at $T_s = 500$ °C.
3. Thermal annealing of as-deposited a-$TiO_2$/Cu films was carried out in vacuum and in oxygen. The nanocrystallization of the a-$TiO_2$/Cu films can be achieved at lower annealing temperatures $T_a$ if the thermal annealing is performed in oxygen.
4. X-ray amorphous a-$TiO_2$/Cu films can strongly differ in final optical properties. The optical properties depend on the magnitude of annealing temperature $T_a$ and the time of thermal annealing $t_a$, i.e. on the energy delivered to the film during thermal annealing process. It means that both $T_a$ and $t_a$ can be used to control the optical properties of the a-$TiO_2$/Cu film.
5. Nanocrystalline anatase nc-$TiO_2$/Cu films exhibit the best hydrophilicity of film surface. These films exhibit low WDCA ($\alpha \approx 20°$) already without UV irradiation.
6. The incorporation of Cu in the $TiO_2$ thin film with anatase structure can results in a strong biocidal activity of the surface of $TiO_2$/Cu film induced by UV irradiation. The efficiency of killing of the *E. coli* bacteria strongly depends on content of Cu in $TiO_2$ film. Strong killing of the *E. coli* was found on the surface of the anatase $TiO_2$/1.5 at.% Cu film irradiated by UV for only 20 min.
7. The surface of anatase $TiO_2$/1.5 at.% Cu film exhibits simultaneously two functions: (1) good hydrophilicity ($\alpha \leq 20°$) and (2) strong killing of *E. coli* bacteria both induced by UV irradiation.

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