Scrittura e tracciamento di materiali radioattivi: una possibile soluzione hi-tech

Il presente articolo descrive la tecnica e gli strumenti per scrivere disegni invisibili su sottili etichette di metalli alcalini terrosi utilizzando una fonte di radiazione nell'estremo ultravioletto. È stato dimostrato sperimentalmente che il nostro metodo di scrittura rende praticamente impossibile la contraffazione di etichette realizzate con una pellicola sottile di fluoruro di litio e offre una protezione molto migliore rispetto alle tecniche anticontraffazione attualmente disponibili. I risultati di test preliminari di esposizione a raggi γ, *x* e β emessi da diversi radionuclidi, quali Co-60, Cs-137, Na-22, e Ba-133, si sono rivelati promettenti per poter usare queste etichette per tracciare materiali radioattivi, al fine di contrastare fenomeni che mettono a rischio la sicurezza, quali ad esempio lo smaltimento e il traffico illecito di scorie radioattive.

Marking and tracking radioactive materials: A possible hi-tech solution

We describe the technique and apparatus to write invisible patterns on thin tags of alkali halides by using an extreme ultraviolet radiation source. We have experimentally demonstrated that lithium fluoride thin-films tags written using this method are almost impossible to counterfeit, and offer a much better protection than the available anti-counterfeiting techniques. The results of preliminary tests of exposure to γ-, *x*- and β-radiation emitted by several radio-nuclides, like Co-60, Cs-137, Na-22, and Ba-133 are promising for the use of these tags to track radioactive materials, in order to fight phenomena impacting security, like the illicit disposal and traffic in radioactive waste.

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Introduction

Counterfeiting is a global problem that has major social and economic consequences [1]. In a recent update [2] the Organization for Economic Co-operation and Development has estimated in USD 250 billion in 2007 the worldwide value of international trade in counterfeit goods, with an impressive growth rate of USD 25 billion/year.
The range of counterfeited products has broadened from luxury objects to products directly impacting on health and safety, like food, pharmaceutical products and automotive/aerospace spare parts, as well as security, like the illegal trade and disposal of radioactive waste coming from both civilian (power plants, hospitals, industries) and military uses.

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As a consequence, anti-counterfeiting (AC) technologies are continuously evolving, extending their applications to identification of the origin of objects or certificates, traceability and identification of paper currency, identity/credit/debit cards, forensic documents, critical/strategic components, dangerous wastes, pharmaceutical products, artworks.
Many AC techniques based on high-tech tagging have been developed, like fluorescent inks (currently used, e.g., in banknotes), thermo-chromic inks, demetallized hot stamping foils, holograms, diffractive foils, laser engraving (writing inside glasses) and radiofrequency identifiers. However, each of these techniques has its own effectiveness and lifetime limited by a variety of factors, including the ability of counterfeiters to replicate the technique, so that a continuous innovation of AC technologies is needed. Moreover, none of the above techniques contemporarily matches a demanding way for a difficult-to-replicate marking and a simple control reading, being at the same time respectful of the privacy issue.
We propose here an invisible marking technology to tag goods/objects whose counterfeiting may impact on both safety and security. After a description of our technology, we present experimental tests to check its application in marking and tracking radioactive materials.

Background

At the ENEA Research Centre in Frascati we have developed expertise in the field of extreme ultraviolet (EUV) and soft *x*-rays generation and applications [3]. In particular, we operated a plasma source driven by two different XeCl excimer lasers. The short-wavelength radiation λ (4 nm < λ <60 nm) emitted by the laser-plasma source is used in different fields, ranging from soft *x*-ray microscopy to radiobiology, from micro-radiography to microelectronics and photonics. Based on our laser-plasma source, we have developed an apparatus for EUV projection lithography, named MET-EGERIA, which is able to print a sub-100-nm-resolution pattern on polymethylmethacrylate (PMMA) resist [4, 5].
Recently, we operated a discharge-produced-plasma source (DPP), which can deliver EUV pulses with energy/solid angle of 20 mJ/ster in the 10-20 nm wavelength spectrum and 60 mJ/sr/shot in the full EUV range, working up to 20 Hz repetition rate [6]. The DPP is particularly suitable to irradiate large-sized targets in the near field with a higher yield vs. laser-plasma source, thus showing its superiority in the EUV contact lithography irradiations.
In specific materials, like alkali halides, EUV radiation can generate electronic point defects, known as "colour centres", which make them luminescent under selective optical pumping [7]. In the case of lithium fluoride (LiF) this modification is permanent at room temperature and the photoluminescence of radiation-induced defects is in the visible spectral range.
Thanks to the very short penetration depth of EUV in most materials, the coloured layer in LiF is so thin (~50 nm) to potentially allow for a very high resolution patterning. A film of LiF can be deposited by thermal evaporation [8] directly on the goods to be protected/traced, or on a tag to be stuck on them. After a suitable EUV irradiation dose, the stored pattern is invisible to the naked eye, and the emitted photoluminescence can be observed only through a suitable optical filter after the colour centres are excited by a spectrally selected illumination.
An example of high-resolution luminescent patterns in a field of about (0.5 x 0.5) mm^2, obtained using a projection EUV microlithography tool, is shown in Figure 1. This is a complex and expensive writing tool, which requires skill and experience in the fields of EUV sources and EUV optics.

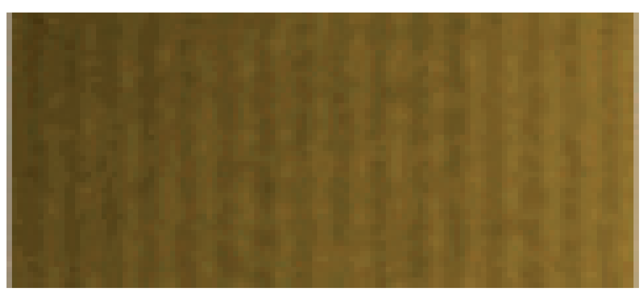

FIGURE 1 Luminescent patterns stored on a LiF film deposited by thermal evaporation on a glass substrate at ENEA [8], obtained by the MET-EGERIA described in [4, 5]. The pattern period is 2.2 micrometers

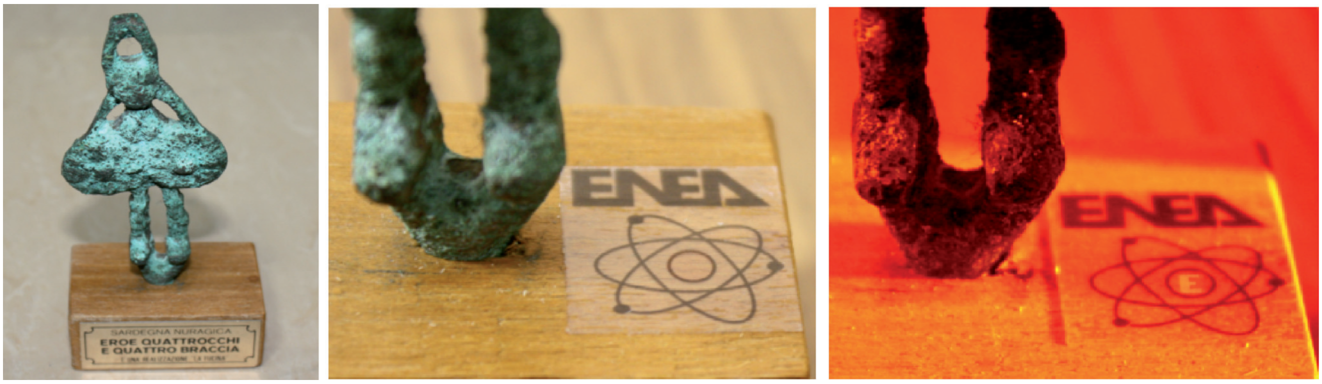

FIGURE 2 Left: Copy of an archaeological bronze statue, known as “hero four-eyes and four-arms”, height: 11 cm; Middle: The transparent and adhesive tag based on a LiF film stuck on the wood base of the statue; Right: The letter ‘E’ patterned by EUV radiation appears when using the patented reading technique
Source: [9]

The invisible marking

Figure 2 shows a LiF film tag patterned by EUV radiation using a contact mask, in this specific case for artwork protection. The letter E becomes visible only by the specific optical excitation and spectrally selected fluorescence spectra.

The apparent similarity with the behaviour of some fluorescent inks fails at a deeper analysis, thanks to the low absorption of colour centres in the ultraviolet, which, on the contrary, is strongly absorbed by most inks, see Figure 3. A simple, differential spectral reading system can thus definitely distinguish between a mark written by our technique and the same mark written by fluorescent ink.

The capability to grow LiF thin films [10] even on plastic substrates allows to develop adhesive tags to stick on the items to be protected and/or traced.

The security level of our technology can be further increased by the digital encoding of the image, by using the current state-of-the-art cryptography techniques. In this case, the control relies not only on the physical reading of the image, but also on its decoding with the appropriate digital key/algorithm [9].

We can further increase the security level of our technology by growing alkali halide films in a series of thin layers, each separated by non-luminescent materials, with a variable tapered thickness. By so doing, after irradiation by ionizing radiation, the energy of the ionizing radiation affects the luminescence ratio of the different layers, and therefore a mark imprinted with an ionizing radiation having a different spectral energy with respect to a pre-determined one can be identified.

ENEA has filed two patents about the invisible marking system [11].

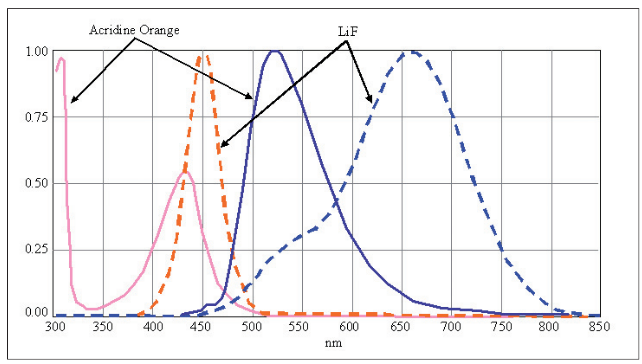

FIGURE 3 Optical absorption and emission spectra of LiF colour centres (dashed lines) and of Acridine orange (continuous lines) in the range 300 nm - 850 nm. Acridine orange is one of the dyes having the most similar absorption and emission spectra vs. LiF
Source: [9]

Is our invisible marking suitable to security-related applications?

In the past, we tested our invisible writing technique to produce AC tags able to protect identity/payment cards and electronic components [12] as well as artworks [9]. Here we discuss the potential use of our technology as identification marks for tracking radioactive substances, which may impact security issues. In fact, a critical field of marking application is related to the traceability of radioactive waste, coming from both civilian (power plants, hospitals, industry) and military uses, in order to trace their origin and then fight the phenomena which impact on security, like their illicit traffic or disposal.

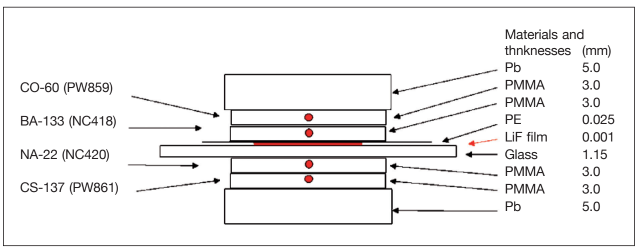

FIGURE 4 Schematic of the irradiation setup of the LiF film patterned with the invisible EUV-marking. The film was sandwiched between several radio-nuclides and exposed to a total dose of 1,700 Gy during 40 days of continuous exposure

Upon request by GIS (Special Intervention Group of Carabinieri military police) we made preliminary irradiation experiments to check if the ionizing radiation emitted by radioactive substances was able to alter the visibility of our marking. To this end, we prepared two LiF thin films deposited on a glass substrate, patterned by irradiation with EUV light through a hexagonal grid. We irradiated one of these films with a total radiation dose of 1.7×10^3 Gy (1 Gy = 1 J/kg) during 40 days of exposure, i.e., with a maximum rate of 1.33 Gy/hour. The exposure was performed by adding γ-, x- and β-radiation contributions from several radio-nuclides, namely Co-60, Ba-133, Na-22, Cs-137. Note that Co-60 and Cs-137 are widely used in industrial radiography (to measure weld and weld overlays, castings, forgings, valves and components, pressure vessels, structural steel, aircraft structures); Co-60 is also used in cancer therapy, whilst Ba-133 is commonly used in manufacturing to measure, e.g., the thickness of metal components and coatings, or the moisture content in manufactured products [13]. In addition, all the above radio-nuclides are used in oil and gas industry [14].
The schematic of the irradiation setup is shown in Figure 4, and the main results are reported in Figure 5, where EUV-marked film is shown before and after irradiation (Figs. 5a and 5b, respectively), as observed by an optical microscope under the same illumination

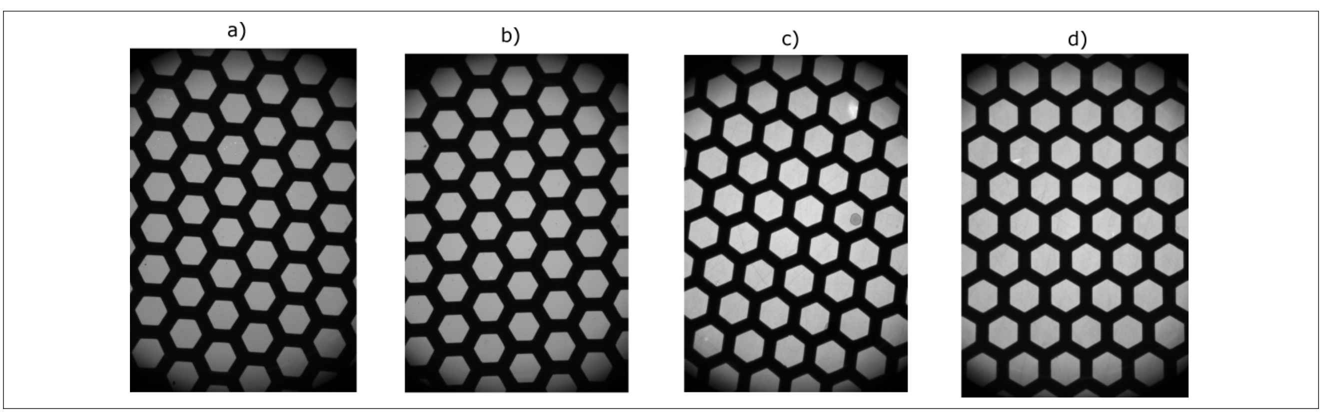

FIGURE 5 Microscope views of the invisible pattern on the LiF films evidenced by the patented reading technique. The period of the hexagonal pattern is about 0.05 mm. From left to right: a) Before irradiation; b) After 40 days of irradiation with a total dose of 1700 Gy; c) Reference sample, not irradiated; d) The same reference sample after 40 days

conditions of a reference unexposed film (see Figs. 5c and 5d).

It appears that the prolonged contact with radioactive materials and consequent exposure did not alter the contrast of the image, and the pattern, still invisible under normal illumination, does not show any detectable difference with respect to the reference pattern on unexposed film (cf. Figs. 5b and 5d).

Accurate and systematic spectral investigations of colour centres in γ-irradiated lithium fluoride thin films in [15, 16] have confirmed that the colour centre photoluminescence generated by a dose of 10^3 Gy is not sufficient to change the contrast of the EUV marking in Figure 5, whilst at a very high dose of 10^6 Gy the photoluminescence of the radiation-induced defects grows to a level that could make it difficult to observe the EUV marking.

Then, a careful choice of the LiF film characteristics (i.e., reducing the film thickness) and an accurate control of their structural, morphological and optical properties are essential to assure the capability of the AC tag behaviour for tracking standard radioactive substances.

Towards the market: durability and production yield

When seeking for security-related uses of our technology, an important issue is the durability of the invisible writing on AC tags. In general, LiF is a rugged material, hard and almost non-hygroscopic. Our tests show that the irradiated LiF films can be touched many times without significantly damaging or altering the visibility of the pattern, as detailed in [12]. When the tags are exposed to severe conditions (heavy and uncontrolled scratching or abrasions), a protecting film can be applied on the tag.

From the production point of view, there are several parameters that influence the number of tags written per unit time, including the time to accurately align the contact masks on tags, the maximum number of tags that can be irradiated in the same run, and the area to be irradiated (which depends on the size of the pattern). When using a commercial EUV source delivering a moderate 100 W average power in the EUV [17], a conservative estimation gives a potential production yield of about 50-100 tags/hour, each tag having a patterned area of 0.4 cm^2.

Conclusions

ENEA has developed and patented a new anti-counterfeiting/tracking technology based on EUV lithography on radiation-sensitive luminescent materials. An arbitrary pattern can be transferred as an invisible image on thin tags based on alkali halides, which in turn can be put on or embedded in any object to be protected or traced. A compact and cheap device can read the luminescent image and check the authenticity and/or the origin of the tags.

Our writing tool is complex and expensive, and requires a skilled team to be optimized. As a consequence, it is highly unlikely that a counterfeiter could build and operate a similar writing tool. On the other hand, the reading system is cheap and simple so that everyone can easily check the presence of invisible patterns to verify if the good is genuine or to check the origin of the material if interested on its tracking.

The complexity and safety level of our hidden patterns can be further enhanced and adjusted by encoding patterns by cryptography techniques, and/or by growing the fluorescent film as a series of thin layers, each separated by non-luminescent materials with variable thickness, as detailed in [11]. The ENEA technology can be used alone, or in conjunction with other anti-counterfeiting/tracing methods.

In previous papers we have demonstrated the feasibility of the application of this technology to artworks [9], to credit/debit cards and electronic components [12], also showing that our AC tags cannot be detached from the original object and stuck on another one, since in this case the pattern becomes visible.

In this paper, we have shown how the exposure of these AC tags with radioactive materials up to a total dose of 1,700 Gy does not alter the contrast of the invisible EUV pattern, see Figure 5. As a consequence, our tags are promising candidates as identification marks for tracking radioactive substances, thus being potentially effective to fight the illicit traffic and disposal of radioactive materials coming from both civilian (power plants, hospitals, industries) and military uses.

As regards the market, a conservative estimation shows that a production of about 50-100 tags/hour can be achieved.

The protection level of our technology can be evaluated by the following standard criteria:

- very high cost to break;
- high probability to detect a clone;
- very low probability of false negatives;
- no privacy risks.

Concerning vulnerabilities, at the moment we are not able to find practical ways to fool the product authentication/tracking.

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