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Invisible Digital Image by Thin-Film Interference of Niobium Oxide Using Its Periodic Repeatability

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SUMMARY There are several benefits of the information that is invisible to the human eye. "Invisible" here means that it can be visualized or quantified when using instruments. For example, it can improve security without compromising product design. We have succeeded in making an invisible digital image on a metal substrate using periodic repeatability by thin-film interference of niobium oxides. Although this digital information is invisible in the visible light wavelength range of 400-800 nm, but detectable in the infrared light that of 800-1150 nm. This technology has a potential to be applied to anti-counterfeiting and traceability.
key words: *niobium oxide, invisible, thin-film interference, interference color, digital information, QR code*

1. Introduction

What is the significance of information that is invisible to the human eye? The invisibility here assumes that the information can be visualized and quantified by instruments. In fact, the advantages of such invisibility are many. For example, invisible digital information embedded on the surface of a product gives anti-counterfeiting effects without damaging the appearance of the product [1]–[3]. There is a potential need for QR codes and barcodes to be invisible on the surface of packaging especially for luxury brand products. Invisibility is also important from a decorative point of view.

Speaking of decoration technology, it is well known that anodic oxidation treatment is performed on metal surfaces to form an oxide film layer on the surface to improve the appearance [4]–[15]. We have been studying the mechanism of coloration by thin film interference using a thin film such as silver sulfide (Ag_2S) on silver plates [16]–[20], titanium oxide (TiO_2) on titanium plates [21] and niobium oxide (Nb_2O_5) on niobium plates [22]–[32]. Thin film interference is the phenomenon that occurs when incident light waves reflected by the upper and lower boundaries of a thin film interfere with one another and they make a new wave. Depending on the optical path length, wavelengths strengthen or weaken each other. The difference in the intensity of reflectance at each wavelength produces color [15].

In the case of niobium oxide on niobium plates, we have observed that similar colors are periodically repeated depending on the thickness of the oxide film. In the case

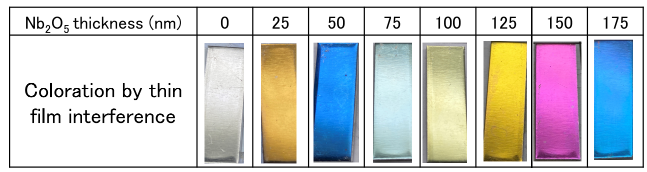

Fig. 1 Color images which exhibit periodic repeatability by thin film interference as a function of the thickness of Nb_2O_5.

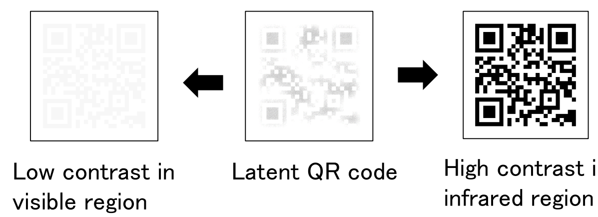

Fig. 2 Concept of invisible QR code.

of the color by thin film interference, the similar colors are repeated periodically depending on the thickness of the niobium oxide layer on the Nb plate. For example, yellow is produced both at 25 and 125 nm, and blue at 50 and 175 nm of the niobium oxide layer, respectively as shown in Fig. 1. This phenomenon suggests that we can make the same color on the niobium plate repeatedly by controlling the thickness of the niobium oxide layer.

More importantly, we found that, when the thickness of niobium oxide is around 90 nm, nearly achromatic color is observed, as in the original niobium substrate [27]. This is because the wavelengths that are strengthened and weakened by thin-film interference of 90 nm niobium oxide are outside the visible light range.

In this present work, we applied this periodic repeatability to invisible digital information. If a 90 nm niobium oxide film could be formed at an arbitrary position on a niobium substrate, it would be possible to form a latent image that is invisible in visible light but detectable in infrared light. For example, it would be possible to form a QR code that is invisible with visible light but detectable with an infrared camera. The concept of the invisible QR code is shown in Fig. 2.

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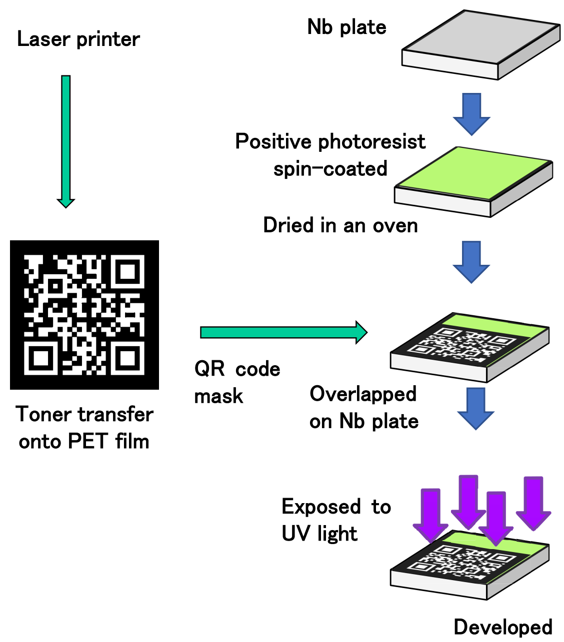


Fig. 3 Preparation of a mask containing QR code information.

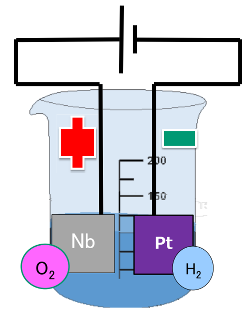


Fig. 4 Schematic diagram showing the electrolysis produces oxygen at the anode and the niobium surface is covered with Nb_2O_5 layer.

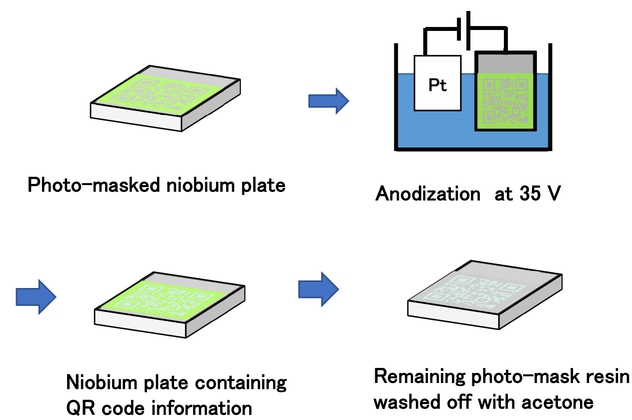


Fig. 5 Preparation of a niobium plate containing QR code information.

2. Experiment

2.1 Formation of Invisible QR Code

The key to achieve an invisible digital image here is how close the color of the niobium oxide thin film on the niobium substrate can be made to the color of the niobium substrate (achromatic color) in the visible light region. The specific method is described below.

The toner was transferred onto a PET film by a laser printer (LP-7010C, Canon) to make a mask for QR code. A positive photoresist solution (FPPR-200, Fuji Chemicals Industrial) was spin-coated on a niobium plate ($30 \times 40 \times 0.1$ mm) and dried in a dry oven. The QR code mask was overlapped on the niobium plate and exposed to ultraviolet light, and then developed as shown in Fig. 3.

We are making the color niobium plate electrochemically by anodizing the plate. Specifically, the electrolysis produces oxygen at the anode and the niobium surface is covered with niobium oxide layer as shown in Fig. 4.

The anodization of the photo-masked niobium plate was carried out using the masked plate as the anode and a platinum-coated titanium electrode (25×35 mm) as the cathode at an applied voltage of 35 V in 5.0 wt.% citric acid solution for 70 sec. This is because the above is the conditions required for making a 90 nm niobium oxide layer.

Finally, the resin remaining on the substrate was washed off with acetone. The process up to this point is summarized in Fig. 5.

The spectral reflectance of niobium plate and anodized niobium was measured with a spectrophotometer V670 (JASCO Corporation). The measurement wavelength ranged from 400-1150 nm.

2.2 Evaluation of Invisible QR Code

A niobium plate with a QR code was photographed with a visible light camera (iPhone 11, Apple) and an infrared monochrome camera with a 940 nm LED (MK-0323, Mintron Enterprise) under an indoor light source. The captured images were displayed on an LCD display (DELL S2240L), and QR code was read using a code reader (iPhone 11, Apple).

3. Results and Discussion

3.1 Formation of Invisible QR Code

We have already found that the thickness of the niobium oxide layer is proportional to the applied voltage [22]. Therefore, the applied voltage can control the thickness of the niobium oxide layer and thus the color. As shown in Fig. 6, when 35 V corresponding to the 90 nm thickness of niobium oxide layer is applied, silver as achromatic color is observed, as in the original niobium plate.

Despite the different thicknesses of niobium oxide layer, the same color can be produced under visible light. On the other hand, there is a possibility that they have different spectra outside of the visible light region. Figure 7 shows the spectra of original niobium and niobium plate with niobium

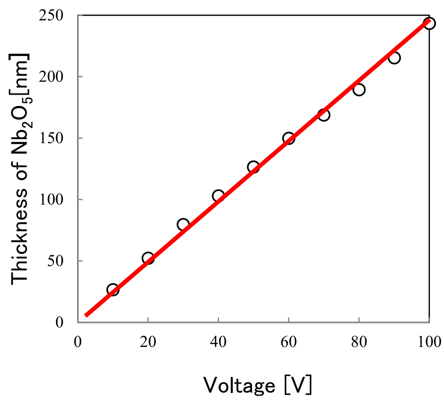


Fig. 6 Thickness of Nb_2O_5 layer as a function of applied voltage.

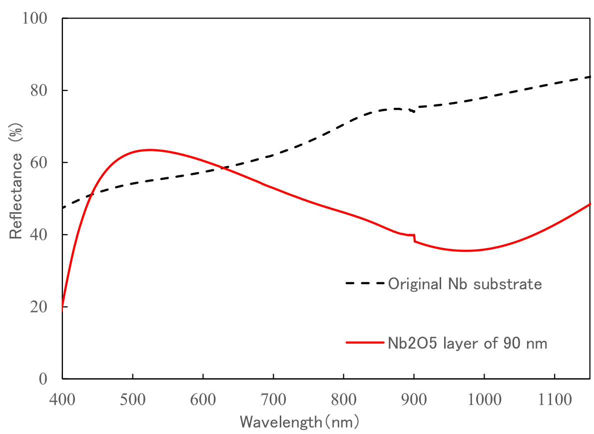


Fig. 7 Spectra of original niobium and Nb with Nb_2O_5 which applied voltage of 35 V in the region from 400-1150 nm.

oxide at 35 V in the wavelength ranged from 400-1150 nm. In the visible region, the reflectance of the spectra of the two samples are not so much different.

This result is consistent with our simulation results which will be published soon [33], [34]. Figure 8 shows the simulated hue of the anodic oxidation when the voltage is increased 5 V step by step. The hue at 35 V is the closest to the origin where the original niobium substrate is located. This figure also shows that the thin-film interference by niobium oxide periodically exhibits similar colors.

On the other, in infrared region, the reflectance of the two samples is clearly different, especially around 1000 nm, the reflectance of the 35 V applied sample is about 40%, while that of the original niobium plate is about 80%.

3.2 Evaluation of Invisible QR Code

Based on the phenomena mentioned above, a 35 V applied niobium oxide layer was successfully formed at arbitrary position on the original niobium plate. We obtained a latent image that is invisible in visible region but detectable in infrared region.

A niobium plate with a latent QR code was photographed by a conventional camera and an infrared camera.

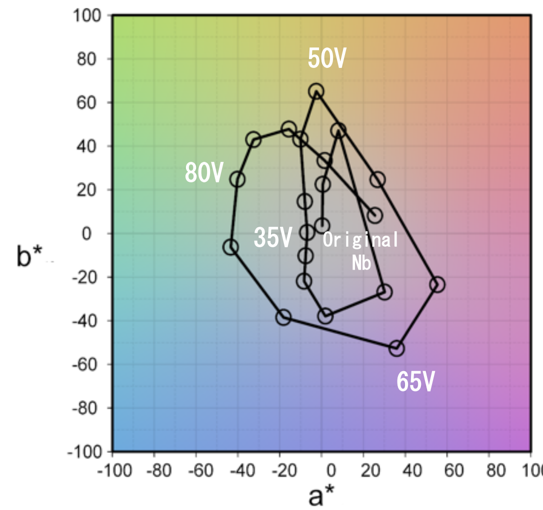


Fig. 8 Simulated hue of the anodic oxidation when the voltage is increased 5 V step by step.

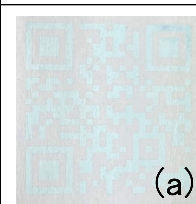
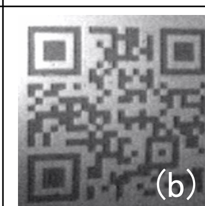
	Conventional camera	Infrared camera
Captured images displayed on LCD	 (a)	 (b)
Readability	×	○

Fig. 9 Niobium plate with a latent QR code photographed by a conventional camera and an infrared camera.

The captured images were displayed on an LCD. The QR code on the niobium plate by the conventional camera was almost invisible due to the low contrast (Fig. 9 (a)). No digital information was read from the QR code. On the other hand, the QR code by the infrared camera has sufficient contrast to be readable, as shown in Fig. 9 (b), and it is possible to jump to an actual homepage. Therefore, it can be said that we obtained QR code that is invisible in the visible light and detectable in the infrared region using thin-film interference of niobium oxides.

This paper focuses on achromatic QR code in achromatic background. We note that, chromatic colors, such as yellow QR code in yellow background, magenta QR code in magenta background, and cyan QR code in cyan background, are also obtained. The details will be reported elsewhere [28].

4. Conclusion

Advantages of these invisible QR codes are summarized as follows.

- Invisible QR codes embedded on the surface of a product gives anti-counterfeiting effects without damaging the appearance of the luxury brand product.
- They can be embedded anywhere on the package. This would allow self-checkout machines to read QR codes without having to check their position.

Therefore, the potential applications of these invisible QR code can be considered to apply anti-counterfeiting and traceability.

We have introduced digital information that is invisible in the visible light range and detectable in the infrared light range using periodic repeatability by thin-film interference of niobium oxides.

These QR code can be expected to apply to anti-counterfeiting, traceability, and other fields. We are currently exploring the industrial application fields.

Company names, system names and product names mentioned herein are trademarks or registered trademarks of the respective companies.

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