Materials Letters 333 (2023) 133701

Contents lists available at ScienceDirect

Materials Letters

journal homepage: www.elsevier.com/locate/matlet

Laser-induced surface plasmon resonance and SERS performance of AgCuAl medium entropy alloy films

H.K. Lin [a,*], Ting-Yuan Li [a,b], I-Chia Chen [a], Y.C. Lo [b]

[a] Department of Materials Engineering, National Pingtung University of Science and Technology, Pingtung, Taiwan
[b] Department of Materials Science and Engineering, National Yang Ming Chiao Tung University, Hsinchu, Taiwan

ARTICLE INFO

Keywords:
Dewetting
Nanoparticle
Surface plasmon resonance
Laser

ABSTRACT

AgCuAl films were deposited on glass substrates using a sputtering system. The films were dewetted using a continuous wave (CW) laser with a wavelength of 1070 nm and various settings of the laser power, duty cycle, and speed, respectively. The results showed that nanoparticles were produced for accumulated energies in the range of 0.1 ~ 2.2 kJ/mm^3. At lower unit volume energies (0.1 ~ 1.3 kJ/mm^3), the particles had a size of around 120 ~ 130 nm. However, as the accumulated energy increased to 1.7 kJ/mm^3, the particle size reduced to 95 nm. The AgCuAl films produced using a duty cycle of 30 % showed an optical absorption peak wavelength in the range of 600 ~ 620 nm. Moreover, a blue shift was observed as the laser power increased as a result of the smaller particle size. AgCuAl nanoparticles (NPs) show a strong Raman scattering effect at 680 cm^{-1} in the presence of melamine solution. Hence, the feasibility of detecting melamine via surface-enhanced Raman spectroscopy was confirmed.

1. Introduction

Nanoparticles (NPs) exhibit many unique properties, including enhanced surface plasmon resonance (SPR) [1], and an antimicrobial performance [2]. The resonant properties of NPs are significantly dependent on their composition, shape and size [3]. The literature contains many studies on Ag, Au, and Cu NPs due to their high stability and strong catalytic performance. High entropy alloys (HEAs) consist of five or more main elements mixed in equimolar proportions [4]. However, some studies have shown that certain medium entropy alloys (MEAs), consisting of just three equiatomic elements, have comparable mechanical properties to HEAs [5]. Dewetting provides a convenient approach for forming NPs on substrates and has the ability to produce NPs in many different thin films [6,7]. The NPs produced by laser-induced dewetting yield an effective widening of the local surface plasmon resonance (LSPR) region [6]. The optical extinction spectra of Ag [8], Cu [7], CuZr [7], and Au [9] nanostructures occurs at wavelengths of 400 ~ 450 nm, 700 nm, 580 nm, and 560 nm, respectively. Surface-enhanced Raman Scattering (SERS) is a rapid and in-time detection technology used in many applications, such as food safety and molecular fingerprint detection [10]. Consequently, the feasibility of utilizing laser-induced dewetting to produce SERS substrates is of significant interest. However, the dewetting of MEAs has seldom been discussed in the literature. Consequently, the effects of the dewetting conditions on the morphologies and SPR response of the resulting AgCuAl films are systematically examined. The practical applicability of the dewetted AgCuAl films is then explored by conducting a Raman spectroscopy analysis of melamine in water.

2. Experiment

AgCuAl films were reported in a previous study [11]. The coatings were then dewetted using a CW laser system (R4 HS Series, SPI) with a wavelength of 1070 nm and a spot size of 19 μm. To investigate the effect of the processing conditions on the formation of NPs, the dewetting process was performed using average laser powers of 15, 20 and 25 W, duty cycles of 30, 50 and 100 %, and scanning speeds of 50, 100 and 300 mm/s. The surface morphologies of the dewetted samples were observed by a Scanning Electron Microscope (JSM-7600F). In addition, the number of particles formed in each sample was quantified using ImageJ software (National Institutes of Health, USA). The optical properties of the dewetted samples were analyzed using a UV–vis-IR spectrophotometer (Lambda 35, PerkinElmer) at wavelengths ranging from 300 ~ 1000 nm. The feasibility of the dewetted films for SERS

* Corresponding author.
E-mail address: HKLin@mail.npust.edu.tw (H.K. Lin).

https://doi.org/10.1016/j.matlet.2022.133701
Received 7 September 2022; Received in revised form 28 November 2022; Accepted 12 December 2022
Available online 15 December 2022
0167-577X/

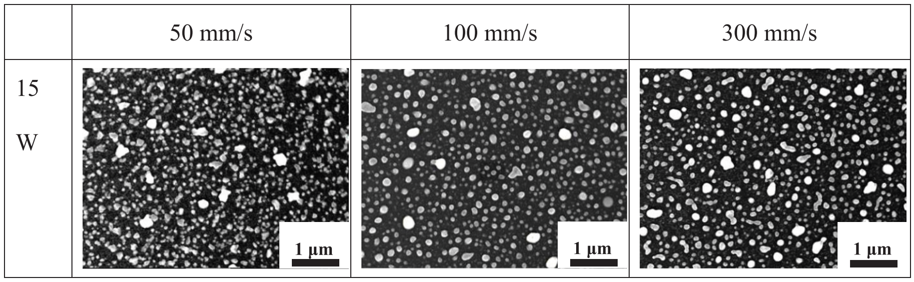

Fig. 1. SEM images and the nanoparticles size distributions of the dewetted AgCuAl films processed by operating with different laser conditions.

detection applications was investigated by dissolving melamine in deionized water to obtain a 1000 ppm solution. The SERS spectra of the melamine solution on the various dewetted AgCuAl surfaces were then acquired by a confocal Raman micro-spectrometer (MRI532S) with a wavelength of 532 nm.

3. Results and discussions

The morphologies of the as-deposited AgCuAl thin films were reported in a previous study [11]. Fig. 1 presents SEM images of the surface morphologies of the dewetted AgCuAl films processed using a constant duty cycle of 30 % and laser powers and speeds in the range of 15 ~ 25 W and 50 ~ 300 mm/s, respectively. At lower laser powers (15 W), the NPs have an irregular shape and have the form of island structures. However, as the laser power increases (20 W), the island structures transform to discrete NPs with a well-rounded shape. According to the particle size analysis in Fig. 1, fixed at 100 mm/s, the average size is 126, 120 and 97 nm for 15 W, 20 W and 25 W, respectively.

The following unit volume energy measure was thus proposed to quantify the dewetting results for the various processing conditions:

$$\text{unit volume energy} = \frac{W}{\pi r^2 * V * dutycycle} \times (\text{overlapping ratio}), \quad (1)$$

where V is the scanning speed, r is the radius of the laser spot, and W is the average laser power. Fig. 2 shows the correlation between the particle size and the unit volume energy for each of the considered duty cycle ratios. For unit volume energies in the range of 0.1 ~ 1.3 kJ/mm^3, the NPs have a relatively constant size of 120 ~ 130 nm. However, for higher unit volume energies of 1.3 ~ 2.2 kJ/mm^3, the NP size varies more widely and has a value of 95 nm at a unit volume energy of 1.7 kJ/mm^3. Overall, the results show that the NP size decreases with an increasing unit volume energy and a decreasing duty cycle.

Fig. 3 shows the absorption spectra of the dewetted AgCuAl films processed using different laser conditions. It is observed that the absorption spectra obtained under higher accumulated energy conditions (25 W) are very different from those obtained under lower energy conditions (15 W). For a duty cycle of 30 %, the peak absorbance wavelength peak reduces from 620 nm to 600 nm as the laser power increases from 20 to 25 W. In other words, a blue shift in the LSPR spectrum occurs as the laser power increases. For a duty cycle of 100 % and scanning speed of 50 mm/s, the absorption spectra show two obvious peaks at around 500 nm and 600 nm, respectively. A similar double-peak absorption spectrum was also reported in a previous study by the present group for AgCu films [12]. The double-peak absorption resulted from the different morphologies with the shape or the different composition of the nanoparticles. According to the above reasons, they can explain the phenomenon about the SPR resonances excitation peaks appear in the two different wavelengths [12,13]. Overall, the results show that the optical properties of the AgCuAl films are highly dependent on the dewetting parameters.

Fig. 4 shows the Raman spectra obtained for the melamine solution when brought into contact with the AgCuAl films processed using different dewetting conditions. In this experiment, the 1000 ppm solution of the melamine places on the AgCuAl nanoparticles films. For each of the films, a strong Raman scattering effect is observed at a wavelength of 680 cm^{-1}. The results are thus consistent with those of previous studies, which reported dominant peaks in the SERS spectra of solid melamine at 584, 676 and 984 cm^{-1}, respectively [14].

4. Conclusions

This study has investigated the formation of NPs on AgCuAl films produced by a CW-laser dewetting process. The results have shown that NPs are formed for unit volume energy values in the range of 0.1 ~ 2.2 kJ/mm^3. For unit volume energies of 0.1 ~ 1.3 kJ/mm^3, the NPs have a uniform size with a mean diameter of approximately 125 nm. However, as the unit volume energy increases to 1.7 kJ/mm^3, the NP size reduces to 95 nm. For a duty cycle of 30 %, the LSPR peak absorbance wavelength undergoes a blue shift from 620 to 600 nm as the laser power increases from 20 to 25 W. However, for a duty cycle of 100 %, the absorption spectra show two obvious peaks at around 500 nm and 600 nm, respectively. Finally, AgCuAl NPs show a strong Raman scattering effect at 680 cm^{-1} in the presence of melamine solution. The practical applicability of the dewetted AgCuAl films explored by conducting a Raman spectroscopy analysis of melamine in water is confirmed.

Author contributions

Prof. Lin conceived of the study, and participated in its design and coordination and drafted the manuscript. Master student T.Y. Li carried out the laser and film studies. Master student I.C. Chen did some microstructure and optical experiments. Prof. Lo participated in the design of the thin film and helped to draft the manuscript. All authors discussed the results and commented on the manuscript. All authors read and approved the final manuscript.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

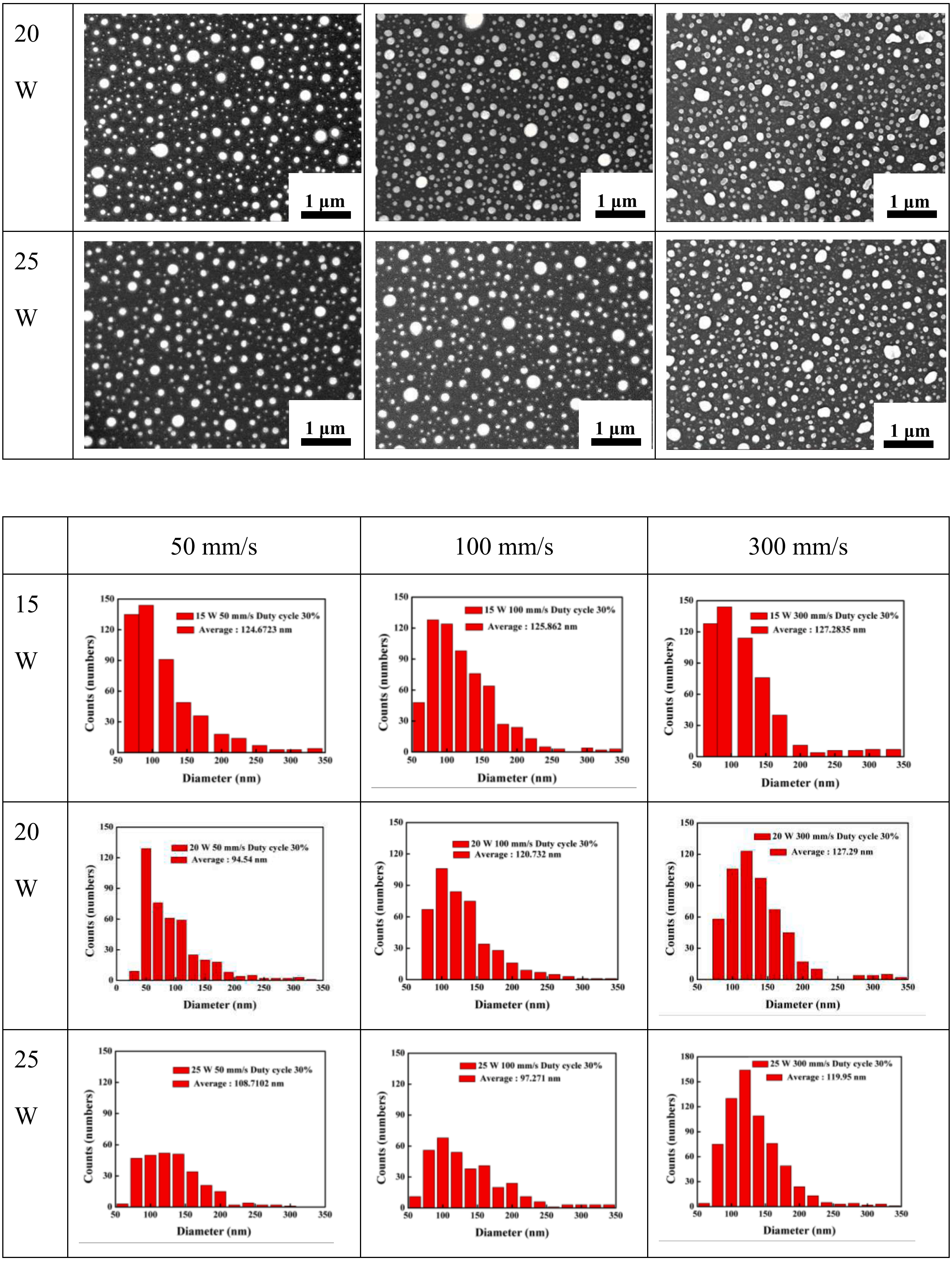

Fig. 1. (*continued*).

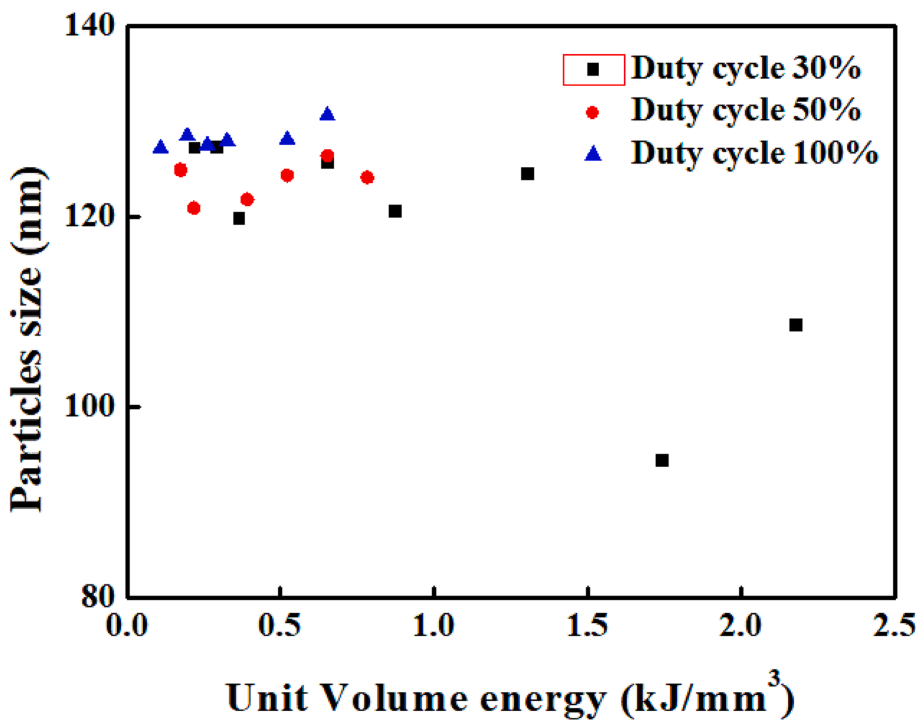

Fig. 2. Effects of unit volume energy on NP particle size under different duty cycles.

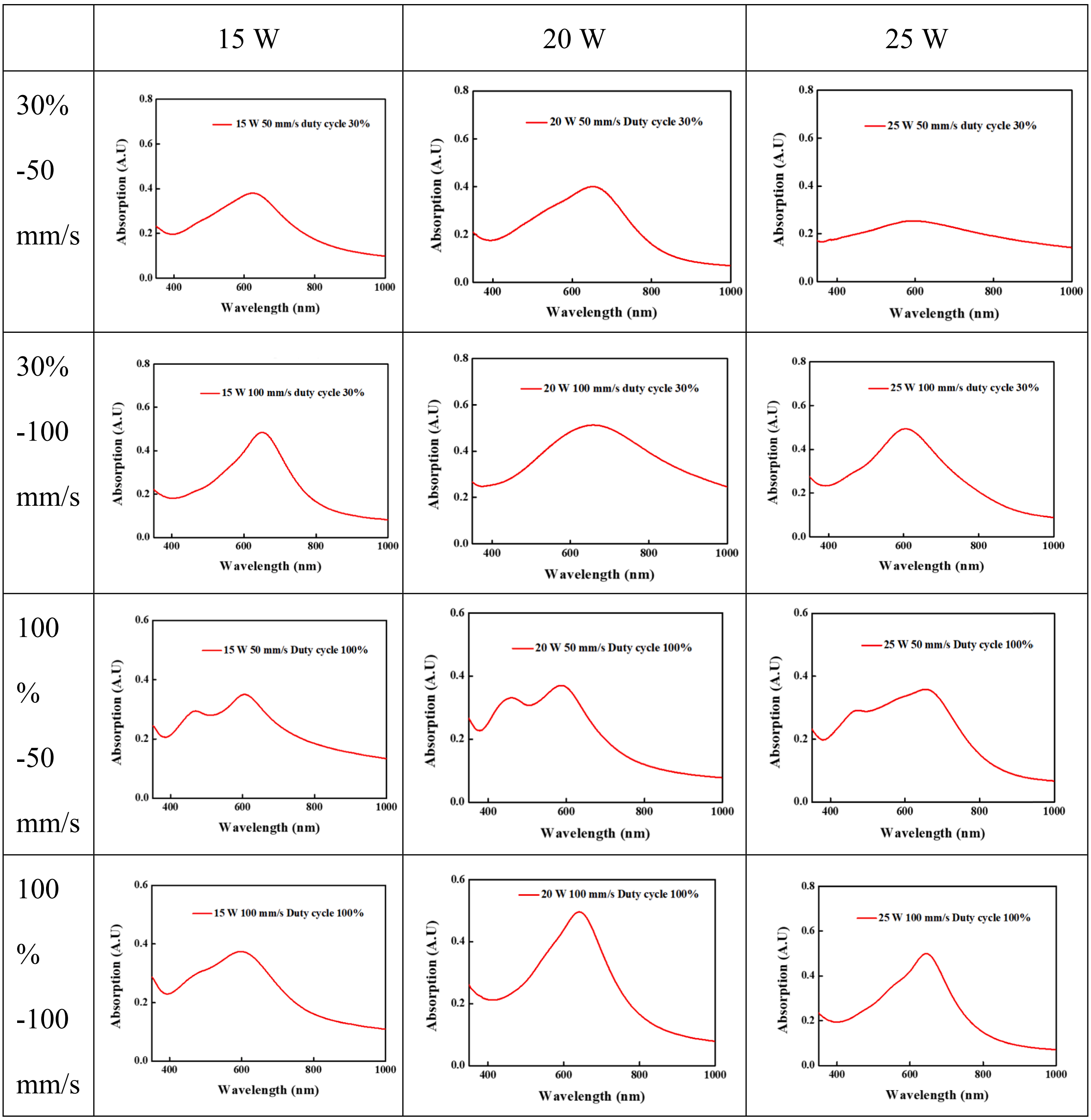

Fig. 3. Absorption spectra of dewetted AgCuAl films processed using different laser conditions.

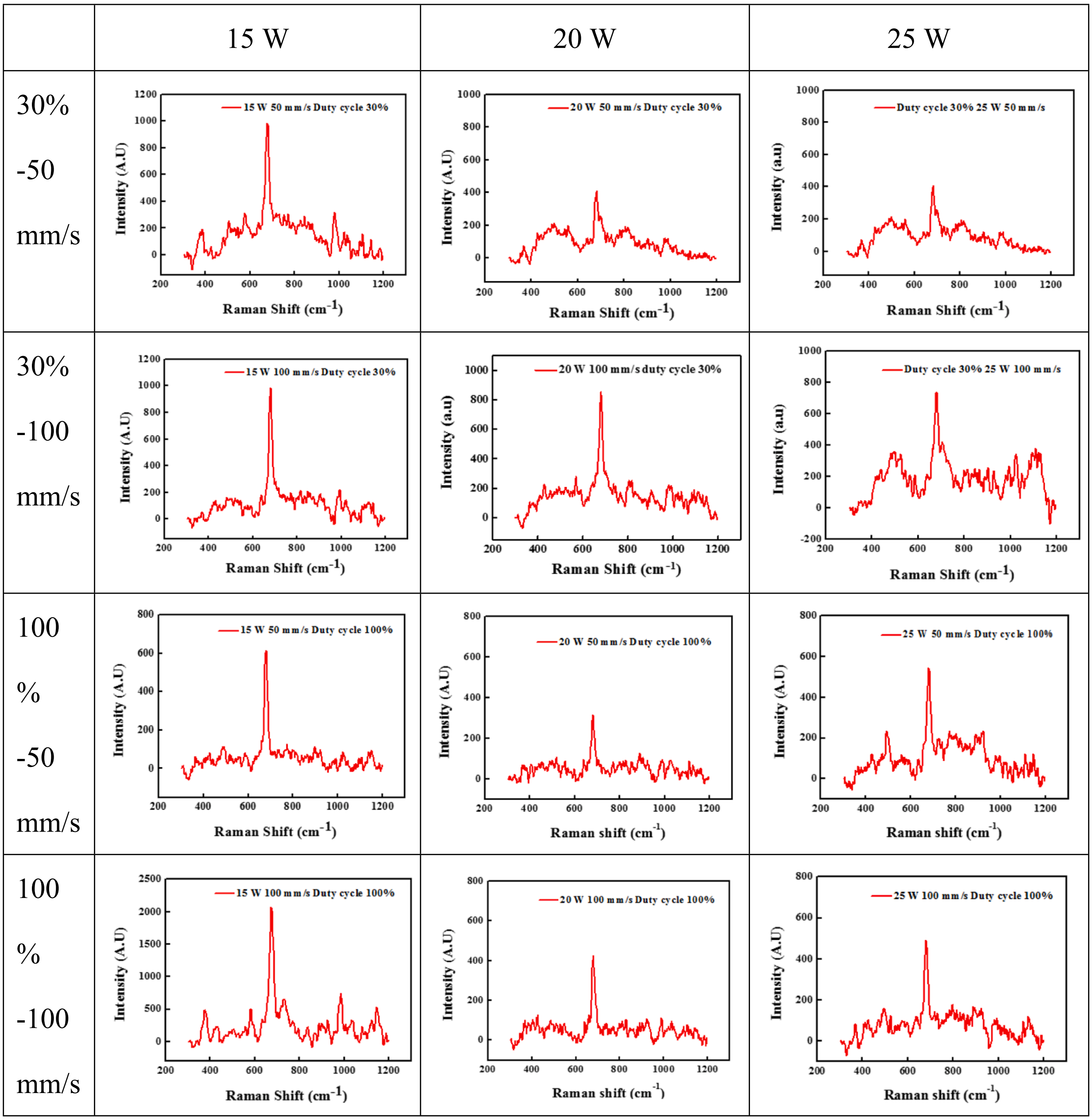

Fig. 4. SERS spectra of melamine on dewetted AgCuAl films processed using different laser conditions.

Acknowledgements

The financial support by the Ministry of Science and Technology of Taiwan, MOST 110-2221-E-020-011.

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