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1. **Draft manuskrip sebelum proses submission**

Identification and analysis of trace metal element on material surface using vaporization technique in pulse CO_2 laser-induced plasma spectroscopy

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Abstract

High-sensitivity analysis of trace element deposited on a material surface has been recently imperative to be carried out especially in material industries. In this study, new technique of laser-induced plasma spectroscopy has been developed and demonstrated by employing vaporization technique for the analysis of trace element on material surface without ablating the material itself. Experimentally, a pulse transversely excited atmospheric CO_2 laser was directed and defocused at +5 mm on a Si surface at inclining degree of approximately 25^o to vaporize the trace metal element from the Si surface to the Pt mesh combined with Cu plate. The vaporized trace metal element then attached and deposited on the mesh surface. The trace metal attached-Pt mesh was then bombarded by focused laser beam to induce a luminous plasma and finally the trace element was identified. Using the present technique, high-sensitivity analysis of Cr as a trace element deposited on the Si surface has been successfully carried out without any ablation of Si surface. Good linear calibration curve of Cr with an intercept zero was produced, which results in limit of detection of Cr of approximately 100 ppb.

Keywords: analysis of trace metal elements; material surface; laser-induced plasma spectroscopy; vaporization technique; pulse TEA CO_2 laser

1. INTRODUCTION

Identification and analysis of trace elements is crucial in laboratories, the environmental field, and industries. In the environmental field, the identification of trace elements in soil has become a topic of interest [1-5]. In materials industries, such as the semiconductor industry, analysis of low-concentration trace elements found on silicon surfaces during the production process has been in high demand [6-10]. Various concentrations of trace contaminants in materials change the characteristics of electricity. Thus, highly sensitive technology is an absolute necessity in order to perform trace metal analysis.

One of standard spectroscopic technique used for the analysis of elements on the surface of material target is X-ray Diffraction Spectroscopy. This technique offers rapid analysis, but the detection sensitivity is quiet low. The sophisticated method recently used for the trace metal analyses in materials is laser-induced plasma spectroscopy (LIPS). The energy source used to induce a luminous plasma in this method is a pulse Nd:YAG laser, and the method has been applied in various analyses of materials [11-15]. The points in favor of this method compared to other conventional spectroscopic methods include its ability to perform rapid identification of elements in a sample without tedious sample

preparation. However, the method cannot be employed easily to conduct high-sensitivity analyses of elements on material surfaces as material ablation occurs when the irradiation of the laser beam takes place on a material surface.

Looking in a different direction, it has been noticed that a peculiar phenomenon occurs when a pulse CO_2 laser is irradiated on the surface of a metal, namely, a high-temperature plasma is produced without any ablation of the metal. This is because the CO_2 laser has a long pulse duration and long wavelength, which results in high plasma absorption [16, 17]. By devising various unique sampling techniques, we employed the gas plasma method to conduct direct analysis in some difficult samples, such as softwoods, powders, and soils [18-20].

We further employed the devised technique successfully in trace metal analysis for a solid material surface of silicon wafer [21]. However, it was confirmed that the technique cannot be used for the sensitive analysis because material ablation of silicon still takes place when the CO_2 laser irradiates the surface of the silicon continuously. In this present paper, we proposed new technique of vaporization utilizing a pulse CO_2 laser in laser-induced plasma spectroscopy for rapid identification and high-sensitivity analysis of trace metal element on material surface. The technique consists of two steps, namely

vaporization and data acquisition. For vaporization, the impurity of trace metal attached on the material surface was vaporized and deposited onto the Pt metal mesh and metal subtarget by defocusing a pulse CO_2 laser beam on the material, which contains trace metal. In the second step, the deposited trace metal elements was then bombarded by a pulse CO_2 laser beam to induce a plasma, obtaining emission spectrum of trace metal element. Using new present technique, rapid identification of trace metal element on material surface can successfully be carried out without damaging the material itself, which is necessary in material industries. The detection sensitivity of impurity element is also high in the order of sub part per million (ppm) level.

2. EXPERIMENTAL PROCEDURE

The material target used in this study was silicon wafers (0.5 mm thick and 51 mm in diameter). The silicon wafers contain Cr at a various concentrations as a trace element on its surface. For example, to produce Cr film at a concentration of 1.25 mg/kg, the same procedure with the previous experiment [21] was conducted. Namely, 1.25 mg/kg of Cr film was made by the homogeneous dilution of 3.53 mg of $K_2Cr_2O_7$ in 1,000 ml of tap water. Tap water was used because Cr particles

can then be deposited easily on the surface of a sample. A solution of 0.01% sugar in liquid was also added to the Cr water to attach the trace element to the surface of the sample strongly. Mixed Cr water (1 mL) was poured subsequently onto the surface of the silicon wafer. The wafer was further heated by an electric heater for 5 minutes so that the Cr trace element was dried completely on the surface of the wafer.

Experimental setup used in this work is illustrated in Fig. 1(a). The setup consisted of two steps, namely new vaporization technique and data acquisition. In vaporization technique, two platinum metal meshes (wire diameter of 0.12 mm and lattice constant of 0.50 mm) were tightly attached on a copper plate with a dimension of 0.1 x 2 x 2 mm^3. The meshes were then placed at 10 mm in front of the Si wafer, which contains impurity on its surface, as illustrated in Fig. 1(a). The Si wafer was placed on a sample holder, which can be rotated during laser bombardment. The transversely excited atmospheric (TEA) CO_2 laser (10.64 um, 200 ns, 750 mJ) was directly defocused at +5 mm by using a ZnTe lens with a focal length of 200 mm onto the Si wafer surface. It should be mentioned that no plasma emission was produced during laser bombardment and only the impurity on the wafer surface is vaporized onto the surface of the Pt metal meshes. During

laser bombardment, the wafer was continuously rotated with a rotation speed of 2 rotations per minute (rpm). This procedure was made to ensure that the laser beam always attaches new position on the wafer surface and therefore, the impurity optimally vaporizes and moves to deposit and accumulate on the mesh surface. For data acquisition, the meshes on which the impurity is deposited, was placed into the alloy chamber with a diameter of 12 cm. During acquisition, the impurity-deposited mesh was rotated with a rotation rate of 2 rpm. He gas (99.999%) was flown into the chamber with a flow rate of 10 L/min. The pressure inside the chamber was kept constant at 1 atmospheric pressure. The pulse TEA CO_2 laser with a laser energy of 1500 mJ was focused on the mesh surface by using ZnTe lens with a focal length of 200 nm. A luminous plasma with a diameter of around 10 mm was then produced just above the mesh surface. The plasma emission was collected by an optical fiber, which the end of the fiber was placed at a distance of 30 mm from the plasma region. The other end of the fiber was fed onto an optical multichannel analyzer system (OMA, ATAGO Macs-320, grating of 1200 groves/mm, 1024-channel detector) to obtain an emission spectrum. Each spectrum obtained in this study was executed by laser irradiation (10 shots). The OMA system was set at 10 μs delay time and 200 μs gate width.

3. RESULTS AND DISCUSSION

Very peculiar phenomenon occurs when a pulse TEA CO_2 laser is directed and focused on a material surface, especially on the metal sample. Namely, a high temperature and big-size plasma was induced without any ablation of the metal surface. The plasma is most often contributed from the surrounding gas, not from the material target, and therefore, we called “gas plasma” as reported in our previous works [17]. By this present method, identification and analysis of impurity in various sample target has been successfully made.

To extend the significance of the method, in this present study, identification of impurity on a material Si surface was made. At initial study, to avoid the ablation of Si itself by a laser bombardment, a platinum metal mesh (wire diameter of 0.12 mm and lattice constant of 0.50 mm) was employed by tight attaching the mesh on the Si surface and by directing a laser beam onto the Si surface at the angle 25^o from the Si surface so that the laser beam does not directly impinge on the Si surface. The pulse TEA CO_2 laser beam (10.64 um, 200 ns, 750 mJ) was further focused onto the surface of Pt mesh at inclining degree of 25^o to induce a luminous plume (Fig. 1(a)). Mixed nitrogen and helium gases with a flow rate of

2.5 liter per minute were flowed during data acquisition pricess. Figure 2 shows an emission spectrum obtained from the silicon surface containing trace metal element of 1.25 ppm Cr at the wavelength region of 410 nm to 440 nm. Typical neutral Cr lines at the wavelength of 425.4 nm, 427.4 nm, and 428.9 nm are clearly identified together with neutral Ca line at 422.6 nm. Furthermore, a high-intensity broaden emission line at 433.8 nm identified as ionic He II line. This result certified that even though the laser beam was sent at the angle of 25^{o} from the Si surface, the Cr impurity deposited on the Si surface still can be vaporized and excited in the plasma region indicated by detection of Cr lines as in the spectrum.

Further experiment was made to confirm whether any ablation happens from the Si surface. As mentioned above, the important goal of the study is to identify and analysis of impurity element on Si surface without any damage on the Si surface. Figure 3 displays an emission spectrum taken from the same condition with Fig. 2 at the wavelength ranging from 270 nm to 310 nm. Neutral atomic Si line at 288.8 faintly appears together with high-intensity neutral He line. The existence of Si line verified that the Si material is still ablated by laser bombardment in the present method. It should be mentioned that when the

inclining degree of the metal mesh to the surface of the Si was reduced from 25^{o} to 10^{o}, the emission line of Si at 288.8 nm significantly decreased and almost disappeared, which stated that the ablation of the Si material also decreased. However, the reduction of the Si ablation also reduces significantly the emission lines of Cr impurity at the wavelength of 325.4 nm, 327.4 nm, and 328.9 nm. Therefore, the present technique is not effective and sensitive to be employed for the detection of impurity deposited on the material surface, especially Si surface.

A new devised technique was then developed to overcome the problem of the material ablation and reduction of the impurity emission lines. The technique consists of two steps as shown in Fig. 1(b). In the first step, a defocused laser beam at +5 mm was sent onto the Si surface to vaporize the impurity from the Si surface to move on the metal mesh. We confirmed that completely no plasma was induced on the Si surface and no Si emission line at 288.8 nm was detected during defocusing of the laser beam. Also, it should be emphasized that no ablation mark on the Si surface was observed by the microscope. In the second step, the impurity deposited-metal mesh and Cu plate was bombarded by the focused laser beam to induce a luminous plasma and to identify the impurity emission. It should be stated that the metal mesh and Cu plate was not ablated by the laser beam because

the power density of the laser beam on their surface is not high enough to ablate the metal as reported in our previous papers [19, 20]. The plasma emission induced was totally contributed from the surrounding gas and the impurity deposited on the surface. We clearly observed the luminous plasma and detected the emission lines of impurity and He gas as shown in Fig. 4. The sample used was Si wafer containing Cr impurity on the Si surface at 4 ppm. Three typical emission lines of neutral Cr at 425.4 nm, 427.4 nm, and 428.9 nm appears with high intensity and quite low background emission even at low concentration of 4 ppm level. These lines are contributed from the trace element of Cr deposited on the Si surface. In addition, high-intensity and broaden emission line of ionic He at 433.8 and neutral Ca line at 422.6 nm contributed from the He surrounding and tap water clearly occurs respectively.

Finally, a semi-quantitative analysis of Cr has been carried out by using the Si sample containing various concentrations of Cr on Si wafer surface. Prior to analysis, reproducibility of the gas emission was examined using the ionic He line at 433.8 nm. As shown in Fig. 5, with the number of laser shots at different places on the surface of metal mesh and Cu plate, on which the Cr impurity was deposited, good reproducibility of the He emission is obtained. This graph

certified that the plasma produced using this present technique is quite stable and therefore it is feasible for the semi-quantitative analysis of Cr trace element in the Si surface. The good reproducibility of the ionic He line at 433.8 nm was then used as a standard line for making the calibration because the He gas has good stability with different concentration of Cr.

Figure 6 displays the calibration curve for Cr in the Si surface. In this graph, Cr line at 425.4 nm was selected because this line has highest intensity compared to other Cr line. Good linearity with zero intercept was obtained between emission ratio of Cr to He and Cr concentration deposited on the Si surface. Using the same equation for calculating the limit of detection (LoD) as reported here [22], the LoD of Cr was estimated to approximately 100 ppb. This result stated that the present vaporization technique has high possibility to be employed for analysis of Cr impurity deposited on the material surface without ablating the material itself.

4. Conclusion

A vaporization technique consisting of two step process utilizing a pulse TEA CO_2 laser has been developed and demonstrated for the identification impurity element of Cr deposited on material surface of Si. Good stability of the plasma emission

was examined. Using the present technique, a semi-quantitative high-sensitivity analysis of Cr impurity deposited on a Si surface without ablating the Si material was successfully made. A good linearity calibration curve of Cr using ionic He line as a standardization with an intercept zero was demonstrated. The limit detection of Cr was approximately 10 ppb. The present technique is potentially applied to high-sensitivity analysis of impurity on material surface in material science and industry.

Acknowledgments

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Figure captions

Fig. 1 Illustration of Experimental setup used in this study (a) by inclining technique, (b) by vaporization technique.

Fig. 2 Emission spectrum of Cr deposited on the surface of silicon wafer containing 1.25 ppm Cr using inclining technique

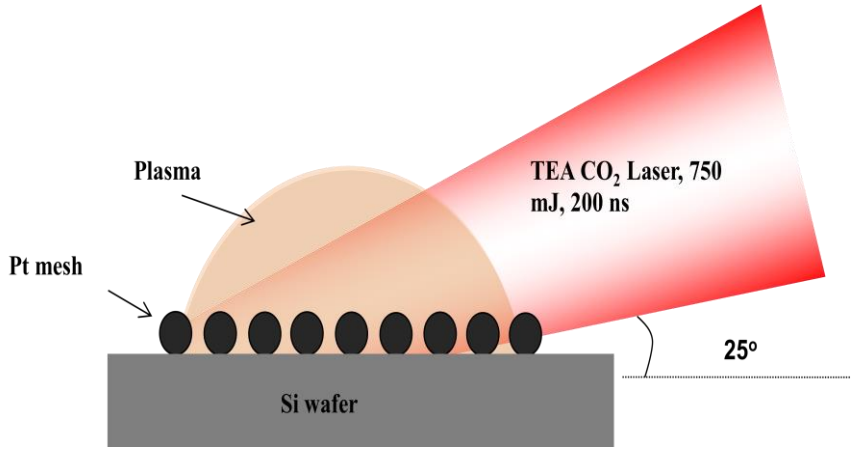
Fig. 3 Emission spectrum of Si taken from the Si wafer containing Cr 1t 1.25 ppm using inclining technique

Fig. 4 Emission spectrum of Cr obtained from the Si wafer surface containing Cr at 4 ppm using vaporization technique

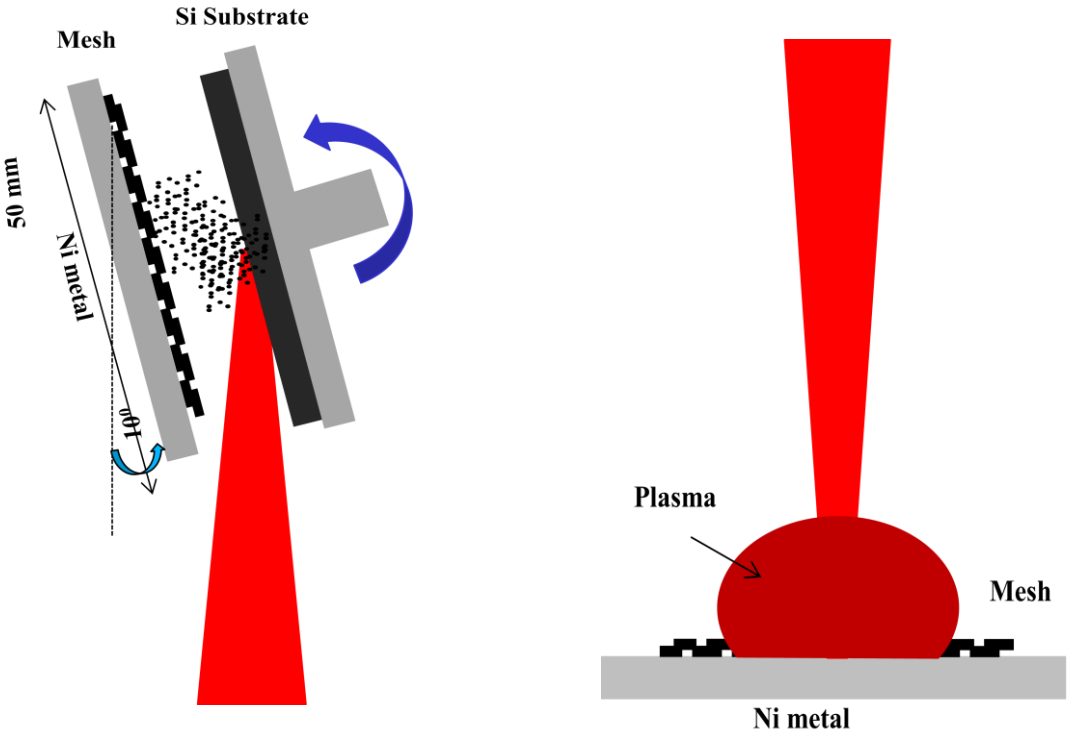
Fig. 5 Reproducibility of He emission obtained from the gas plasma produced on the surface of Si wafer containing 4 ppm Cr

Fig. 6 Calibration curve of Cr deposited on the Si surface at various concentrations by using the vaporization technique

Figure 1
Experimental setup used in this study



(a)



(b)

Figure 2
Emission spectrum of Cr deposited on a surface of silicon wafer containing 1.25 ppm Cr

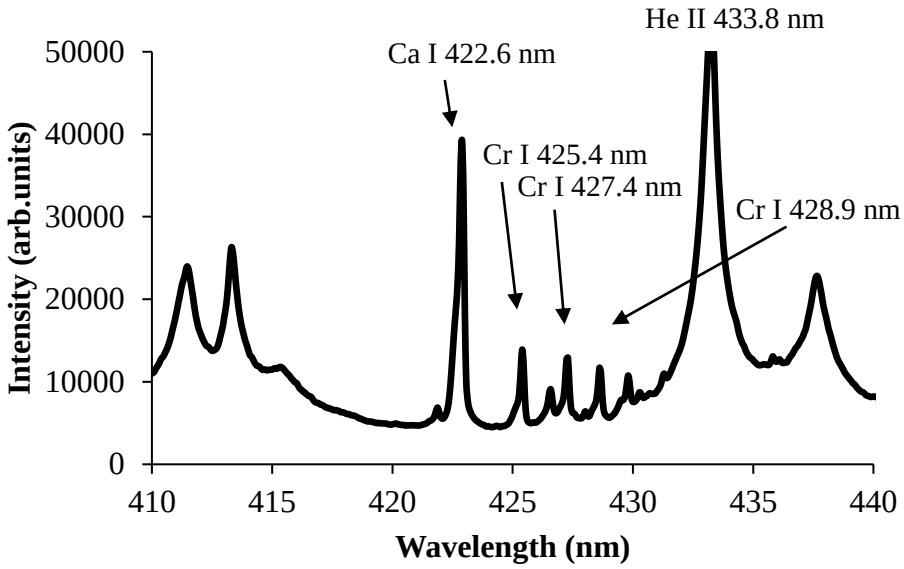


Figure 3

Emission spectrum of Si taken from the Si wafer containing Cr at 1.25 ppm

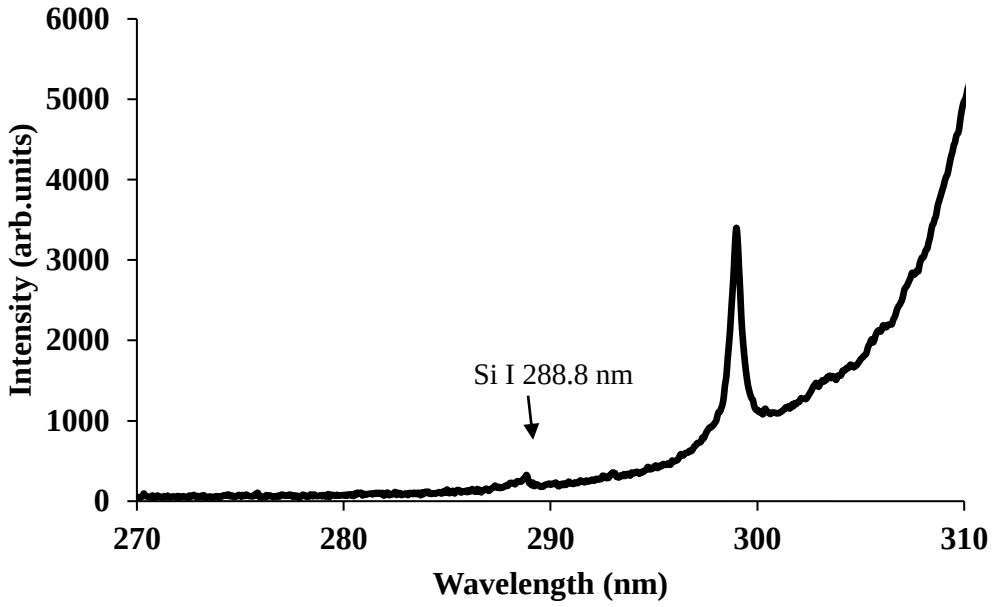


Figure 4

Emission spectrum of Cr obtained from the Si wafer surface containing Cr at 4 ppm using vaporization technique.

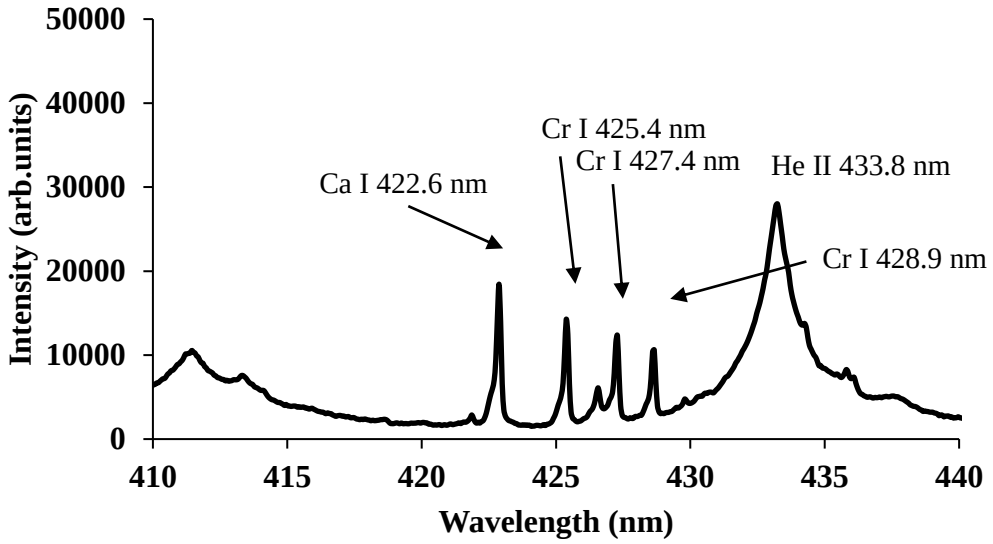


Figure 5

Reproducibility of He emission obtained from the gas plasma produced on the surface of Si wafer containing 4 ppm Cr.

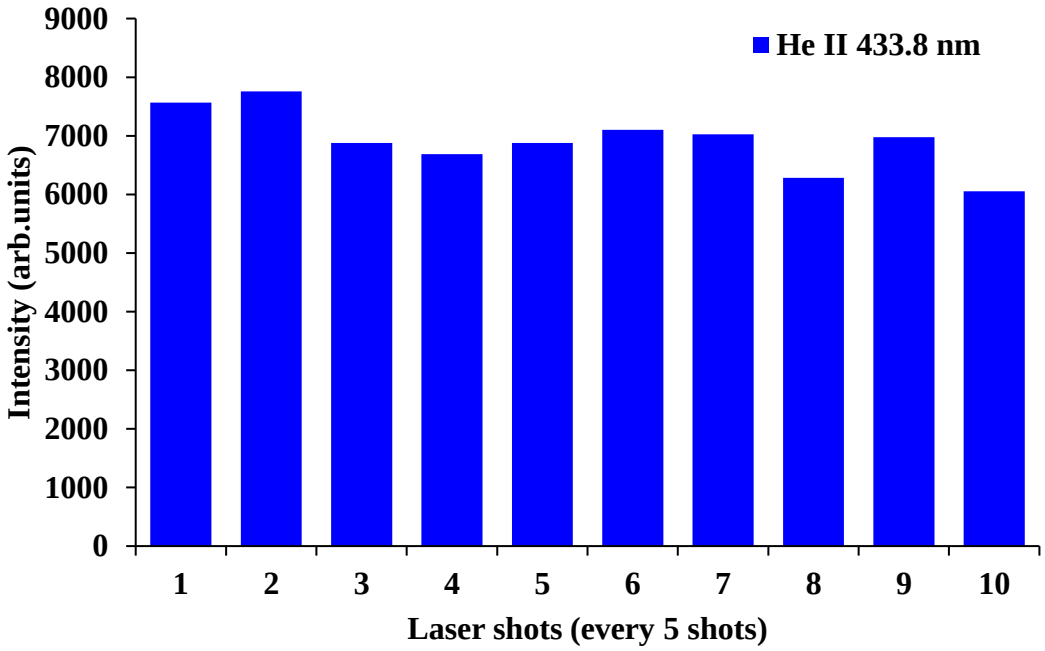
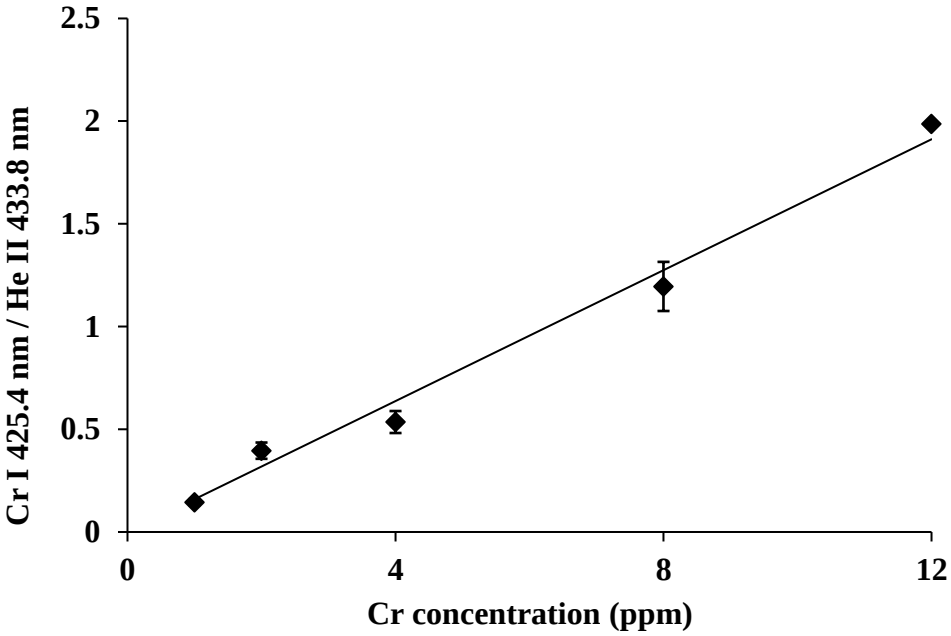


Figure 6

Calibration curve of Cr deposited on the Si surface at various concentrations by using the vaporization technique



2. **Submission acknowledgment dari Heliyon (8 Mei 2020)**

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other minor comments are following:
(1) The author mentioned in the Introduction section that X-ray Diffraction Spectroscopy is one of the standard technique for the surface analysis. X-ray photoelectron Spectroscopy (XPS) is more appropriate technique for surface analysis.
(2) The limit of detection of Cr is given 10 ppb in Conclusion section while it is 100 ppb in all other sections.
(3) A little detail about calculation of limit of detection should be given. At least an equation.
(4) Authors should also mention more latest references on the trace elements detection using LIBS.

Reviewer #2: Methods: It is fine.

Results: It is fine

Interpretation: ok.

Other comments: ok

Reviewer #3: Methods:

Results:

Interpretation:

Other comments: Please see my summary that addresses all three aspects above

Reviewer #4: Methods:

Results:

Interpretation:

Other comments:The paper presents an experimental work for the detection of Cr by CO2 laser induced plasma on the surface of in silicon substrate by emission spectroscopy. A New technique of laser-induced plasma spectroscopy has been developed and demonstrated. A vaporization technique consisting of two-step process utilizing a pulse TEA CO2 laser has been developed and demonstrated for the identification impurity element of Cr deposited on material surface of Si. A good linearity calibration curve of Cr using ionic He line as a standardization with an intercept zero was demonstrated. The limit detection of Cr was approximately 100 ppb.
The paper is well written and the results are well presented. I recommend it for publication after answering the questions and with minor mandatory corrections and comments that should be taken into consideration.
Why the authors are using the name laser induced plasma spectroscopy? They should use laser induced breakdown spectroscopy LIBS. It is commonly admitted by the LIBS community and most journals the use of LIBS rather than LIPS.
What is the purpose of using deposit to do the analysis and not directly fire on the sample?
Figure 3 showing weak line of 288.16nm it is not because the low concentration of Si it is indeed the response of their experimental setup which is probably not sensitive in the UV. Did you check the 390.5nm which is not as intense as 288.1 but still strong to be detected.
Figure 2 the Helium lines looks saturated what is the dynamic range of their ICCD?.
Some minor comments:
Page4 line 25 characteristics of electricity should be changed to appropriate word for electrical conduction or another word.
Page 4 Line 43 use LIBS instead of LIPS
Page 7 line 36 ZnTe lens with a focal length of 200 mm and not nm
In the conclusion, the LOD should be 100ppb and not 10 ppb.

Reviewer #5: Methods:

Results:

Interpretation:

Other comments: The use of the language needs some revisions.

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4. Balasan komentar Editor dan Reviewers

Manuscript. Number.: HELIYON-D-20-02852
Title: Identification and analysis of trace metal element on material surface using vaporization technique in pulse CO2 laser-induced plasma spectroscopy

Dear Editor in Chief
Heliyon

Thank you very much for reviewing our paper entitled “Identification and analysis of trace metal element on material surface using vaporization technique in pulse CO_2 laser-induced plasma spectroscopy”, which we have submitted to Heliyon Journal.

We have completely read your letter and feel happy that our manuscript is suitable for publication in Heliyon Journal after appropriate revisions.

In this letter, we would like to respond the comments from reviewers as below. Considering the comments from reviewers, we have made a final revision in our manuscript. The revision parts are shown in the revised manuscript using red letter.

We would like to thank you very much for your kindness.

Best regards
Ali Khumaeni et al.

Reviewer #1:

Reviewer point #1: However, I have one query regarding delay time. Why authors selected a delay time of 10 micro second for plasma emission studies?
Author response #1: For plasma emission studies, a delay time was selected at 10 μs. This is because in laser plasma induced by a pulse TEA CO_2 laser (10.64 um, 200 ns, 1500 mJ), the best spectral quality, namely narrow full width at half-maximum (FWHM) and optimum signal to noise (S/N) ratio with low background continuum emission is obtained at around 10 μs. Below 10 μs, the FWHM is still quiet wide and background continuum is still high. The background continuum emission, which is produced by Bremsstrahlung effect (free-free) and recombination (free-bound transition), has long lifetime up to around 10 μs compared to that of plasma emission produced by Nd:YAG laser, which has background continuum emission up to around 1 μs. In laser-induced breakdown spectroscopy (LIBS), FWHM of emission line, S/N ratio, and background emission determine the spectral quality and thus influence the sensitivity. Therefore, the delay time of OMA system was set at 10 micro second to remove the background emission.
We have included this explanation in the revised manuscript, Experimental procedure section, end of paragraph 2.

Reviewer point #2: The author mentioned in the Introduction section that X-ray Diffraction Spectroscopy is one of the standard technique for the surface analysis. X-ray photoelectron Spectroscopy (XPS) is more appropriate technique for surface analysis.
Author response #2: We agreed with reviewers. We replaced X-ray photoelectron spectroscopy (XPS) as a standard technique for elemental analysis on material surface as shown in the revised manuscript, Introduction section, beginning of paragraph 2.

Reviewer point #3: The limit of detection of Cr is given 10 ppb in Conclusion section while it is 100 ppb in all other sections.
Author response #3: We made a miswriting. We have revised that the limit detection of Cr is 100 ppb as shown in the revised manuscript, Conclusion section.

Reviewer point #4: A little detail about calculation of limit of detection should be given. At least an equation.
Author response #4: The limit of detection was obtained by calculating the signal concentration which yielded 3 times the noise level because this was clearly identified as a signal that could be distinguished from the noise. We have added this additional information to calculate the limit of detection in the revised manuscript, Results and discussion section, last paragraph.

Reviewer point #5: Authors should also mention more latest references on the trace elements detection using LIBS.
Author response #5: We added some latest references on the trace element detection using LIBS as shown in the revised manuscript, Introduction section, Paragraph 3.

Reviewer #2:

Reviewer #1: Methods: It is fine.
Author response #1: Thank you very much for your positive review of our manuscript submitted to Heliyon Journal

Results: It is fine
Author response #2: Thank you very much for your positive review of our manuscript submitted to Heliyon Journal

Interpretation: ok.
Author response #3: Thank you very much for your positive review of our manuscript submitted to Heliyon Journal

Other comments: ok
Author response #4: Thank you very much for your positive review of our manuscript submitted to Heliyon Journal

Reviewer #3:

Methods:
Author response #1: Thank you very much for your positive review of our manuscript submitted to Heliyon Journal

Results:
Author response #2: Thank you very much for your positive review of our manuscript submitted to Heliyon Journal

Interpretation:
Author response #3: Thank you very much for your positive review of our manuscript submitted to Heliyon Journal

Reviewer point #4: page 4 lines 14 – 27 state "…a high-temperature plasma is produced without any ablation of the metal." However, that statement appears to be unsubstantiated.
Author response #4: We have changed the sentence in the revised manuscript (Introduction section, paragraph 5) to be it has been noticed that a peculiar phenomenon occurs when a pulse CO_2 laser is irradiated on the surface of a metal, namely, a luminous plasma is produced with a large-volume.

Reviewer point #5: The article appears to use a double-pulse arrangement, but without referencing some references.
Author response #5: We have shortly discussed and cited some papers of double pulse arrangement as in the revised manuscript, Introduction section, paragraph 4.

Reviewer point #6: On page 5, there is mention of vaporization. I understand that the "vaporized" material corresponds to ablated material, but on page 4, it is stated that a high-temperature plasma causes no ablation – this apparent contradiction needs to be resolved
Author response #6: There is different meaning between term vaporized material and ablated material. The term vaporized material is used to explain the vaporization of impurity deposited on material surface/silicon surface without any ablation of the material/Si itself. Thus, only impurity deposited on the material surface will vaporize due to the bombardment of defocused laser beam. While, the term of ablated material means the material itself (Si) will ablate when the laser beam was focused on the material surface. Therefore, there is difference between term vaporized material and ablated material.

Reviewer point #7: Figure 3: Did you calibrate the recorded data for spectral sensitivity? Also, please indicate how you would justify "high" temperature plasma, and what do you mean by "high."
Author response #7: In Fig. 3, we did not quantify the sensitivity because in this figure, we only confirm whether any ablation of the material (namely Si material) when we used the technique in Fig. 1(a). The spectrum shows the emission line of Si appears at 288.8 nm. Therefore this technique of Fig. 1(a) is not possible to be used for impurity analysis without damaging the material itself. we have removed the term high in "temperature plasma". However, we have justified and calculated the

electron temperature in the plasma, namely the temperature is around 5000 K, as written in the revised manuscript.

Reviewer point #8: There are quite a few edits regarding use of English, especially use of articles.
Author response #8: we have asked a professional proofread company to edit the grammar of the manuscript.

Reviewer point #9: It will help to clarify/calculate the irradiances of the first and second beams.
Author response #9: We have calculated the irradiance of the first and second laser beams. Based on our calculation, the irradiance of the first and second laser beam are 0.09 GW/cm^3 and 0.75 GW/cm^3. We have included the irradiance of laser beam in revised manuscript, Experimental procedure section.

Reviewer point #10: It will also help to reference International Journal of Spectroscopy, Volume 2010 |Article ID 593820 | 7 pages | https://doi.org/10.1155/2010/593820 and put your work in context with optical emission spectroscopy following laser-induced breakdown.
Author response #10: we have included additional references as your suggestion in the revised manuscript, Introduction section, paragraph 3.

Reviewer point #11: Please determine electron temperature and density from your data, possibly you also have data for hydrogen lines from the Balmer series. Figure 4, please re-evaluate your wavelength calibration: Is it possible that the lines near 410 and 434 are indeed hydrogen Balmer series lines? Also, is this spectrum calibrated for sensitivity?
Author response #11: Following your suggestion, we analyzed again Fig. 4 and we made a misreading at wavelength 410.2 nm and 434.0 nm, which are actually hydrogen lines H_δ and H_γ respectively. We have revised the spectrum in Fig. 4, namely we replace He II 433.8 nm to H_γ 434.0 nm and added information H_δ 410.2 nm. Furthermore, we have also determined the electron temperature and electron density from H lines in our data. Based on our calculation, the electron temperature is estimated to be around 5000 k and the electron density is around 10^{17} cm$^{-3.}$ We have included this information in the revised manuscript, Results and discussion section, paragraph 4.

Reviewer point #12: Overall, there are several aspects in this manuscript that would need to be addressed prior to considering the presentation. I would recommend significant edits, specifically resolving the apparent contradiction. Furthermore, I recommend to focus on applications but include several numbers that describe the plasma. If possible, address some plasma characteristics during the first 10 microseconds.
Author response #12: we have made significant edit following your suggestion. Furthermore, we have also clarified the contradiction and revised the contradiction as in the revised manuscript. In this present we did not describe the characteristics of plasma during first 10 μs because we focus to use the present technique and produced plasma for semi quantitative application. We will discuss in the near future paper about the specific characteristics of plasma at initial plasma to study deeply the process of plasma generation especially using pulse TEA CO_2 laser.

Reviewer #4:

Reviewer #4: Methods:
Author response #1: Thank you very much for your positive review of our manuscript submitted to Heliyon Journal

Results:
Author response #2: Thank you very much for your positive review of our manuscript submitted to Heliyon Journal

Interpretation:
Author response #3: Thank you very much for your positive review of our manuscript submitted to Heliyon Journal

Reviewer point #4: Why the authors are using the name laser induced plasma spectroscopy?
Author response #4: We agreed with reviewer. We have changed the name laser induced plasma spectroscopy to laser induced breakdown spectroscopy (LIBS), which is generally used in the field of LIBS in the revised manuscript.

Reviewer point #5: What is the purpose of using deposit to do the analysis and not directly fire on the sample?
Author response #5: The purpose of the study is to perform rapid identification of trace metal element on material surface without damaging the material itself, which is necessary in material industries. To this end, we proposed new technique consisting of two steps, namely vaporization and data acquisition. Namely, firstly, we vaporized and deposited trace elements from the material surface onto Pt mesh and metal subtarget surface. Subsequently, the laser beam was bombarded on the Pt mesh to induce a plasma, obtaining emission spectrum of trace metal element. We did not directly fire the laser beam on the sample surface because If we directly fired the laser on the solid material sample (Si), the material will ablate and thus damaging the material itself.

Reviewer point #6: Figure 3 showing weak line of 288.16 nm it is not because the low concentration of Si it is indeed the response of their experimental setup which is probably not sensitive in the UV. Did you check the 390.5 nm which is not as intense as 288.1 but still strong to be detected.
Author response #6: We agreed with reviewer that weak line of 288.16 nm is not because the low concentration of Si, whereas we used Si wafer, which contains dominant Si atom. Our experimental setup is still sensitive in this UV region proven by high emission intensity of Si at 288.16 nm when we directly irradiated pulse laser onto Si surface. The weak line of Si 288.16 nm is most often because of new experimental setup, which we proposed in this study, namely, by inclining the laser beam at inclining degree of 25^{o}coming onto the Si surface, which is attached by a metal mesh just on the Si surface. This new setup can effectively reduce sample ablation due to shadow effect by a metal mesh as reported in our previous paper (Ali Khumaeni et.al., Journal of Modern Optics). We did not check the 390.5 nm line because our setup is still sensitive at UV region especially to detect Si line at 288.16

nm. We have included this explanation in the revised manuscript, Results and discussion session, paragraph 3.

Reviewer point #7: Figure 2 the Helium lines looks saturated what is the dynamic range of their ICCD?.
Author response #7: We have misread the emission line at 434.0 nm. This line is not He line, but it is H_γ 434.0 nm. In the study, we used OMA system (ATAGO Macs-320) consisting of a 0.32-m focallength spectrograph with a grating of 1,200 groves/mm, a 1024-channel photodiode detector array, and a microchannel plate image intensifier to detect the laser plasma radiation. The spectral resolution of the OMA system is 0.2 nm. The maximum intensity of emission spectrum can be adjusted by changing image intensified (II) OMA system. In this study, we focused on emission lines of Cr identified in the spectrum at the wavelength of 425.4 nm, 427.4 nm, 428.9 nm using inclining technique.

Reviewer point #8: Page4 line 25 characteristics of electricity should be changed to appropriate word for electrical conduction or another word
Author response #8: We agreed with your suggestion. We have changed the term to be electrical conduction as in the revised manuscript, Introduction section, paragraph 1.

Reviewer point #9: Page 4 Line 43 use LIBS instead of LIPS
Author response #9. We agreed with your suggestion. We have changed LIPS to LIBS in the revised manuscript.

Reviewer point #10: Page 7 line 36 ZnTe lens with a focal length of 200 mm and not nm
Author response #10: Thank you for your revision. This is miswriting. We have changed the focal length of ZnTe lens to be 200 mm as in the revised manuscript.

Reviewer point #11: In the conclusion, the LOD should be 100 ppb and not 10 ppb.
Author response #11: Thank you for your revision. This is miswriting. We have changed the LoD to be 100 ppb.

Reviewer #5:

Reviewer #5: Methods:
Author response #1: Thank you very much for your positive review of our manuscript submitted to Heliyon Journal

Results:
Author response #2: Thank you very much for your positive review of our manuscript submitted to Heliyon Journal

Interpretation:
Author response #3: Thank you very much for your positive review of our manuscript submitted to Heliyon Journal

Other comments: The use of the language needs some revisions.
Author response #4: We have revised the language. Final revision is shown in revised manuscript.

5. **Paper setelah proses revisi mempertimbangkan masukan Editor dan Reviewers**

Identification and analysis of trace metal element on material surface using pulse CO_2 laser-induced breakdown spectroscopy applying vaporization technique

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Abstract

High-sensitivity analysis of trace element deposited on a material surface has been recently imperative to be carried out especially in material industries. In this study, new technique of laser-induced breakdown spectroscopy has been developed and demonstrated by employing vaporization technique for the analysis of trace element on material surface without ablating the material itself. Experimentally, a pulse transversely excited atmospheric CO_2 laser was directed and defocused at +5 mm on a Si surface at inclining degree of approximately 25^o to vaporize the trace metal element from the Si surface to the Pt mesh combined with Cu plate. The vaporized trace metal element then attached and deposited on the mesh surface. The trace metal attached-Pt mesh was then bombarded by focused laser beam to induce a luminous plasma and finally the trace element was identified. Using the present technique, high-sensitivity analysis of Cr as a trace element deposited on the Si surface has been successfully carried out without any ablation of Si surface. Good linear calibration curve of Cr with an intercept zero was produced, which results in limit of detection of Cr of approximately 100 ppb.

Keywords: analysis of trace metal elements; material surface; laser-induced breakdown spectroscopy; vaporization technique; pulse TEA CO_2 laser

1. INTRODUCTION

Identification and analysis of trace elements is crucial in laboratories, the environmental field, and industries. In the environmental field, the identification of trace elements in soil has become a topic of interest [1-5]. In materials industries, such as the semiconductor industry, analysis of low-concentration trace elements found on silicon surfaces during the production process has been in high demand [6-10]. Various concentrations of trace contaminants in materials change the electrical conduction. Thus, highly sensitive technology is an absolute necessity in order to perform trace metal analysis.

One of standard spectroscopic techniques used for the analysis of elements on the surface of material target is X-ray Photoelectron Spectroscopy (XPS). This technique is based on the photoelectric effect, which is able to identify the elements present within a material. XPS has been applied to identify elements in inorganic compound, metal alloys, and semiconductors [11-14]. The other technique for the analysis of elements on the surface of material target is X-ray Diffraction Spectroscopy (XRD) [15-16]. This technique offers rapid analysis, but the detection sensitivity is quiet low.

The sophisticated method recently used for the trace metal analyses in

materials is laser-induced breakdown spectroscopy (LIBS). The energy source used to induce a luminous plasma in this method is generally a pulse Nd:YAG laser [17-19]. Some researchers used pulse CO_2 laser as an energy source to effectively induce a luminous plasma, which has long lifetime and large volume [20-22]. The LIBS method based on Nd:YAG and CO_2 lasers has been applied in various analyses of materials [23-26]. Recently, the LIBS system has been employed for analysis of trace elements in liquids and semiconductors [27-29]. The points in favor of this method compared to other conventional spectroscopic methods include its ability to perform rapid identification of elements in a sample without tedious sample preparation. However, the method cannot be employed easily to conduct high-sensitivity analyses of elements on material surfaces as material ablation occurs when the irradiation of the laser beam takes place on a material surface.

To improve the detection sensitivity, some researchers employed double pulse laser induced breakdown spectroscopy (DP-LIBS), in which one laser is used to induce an initial plasma and the remaining one is functioned to reheat the plasma induced by first laser [30-33]. This technique has been applied to analysis of various materials including metals and semiconductors [34-35]. However, based

on our experience, the use of DP-LIBS for elemental analysis is tedious in experimental preparation and quiet expensive due to requirement of additional laser system [36].

Looking in a different direction, it has been noticed that a peculiar phenomenon occurs when a pulse CO_2 laser is irradiated on the surface of a metal, namely, a luminous plasma is produced with a large-volume and long lifetime. This is because the CO_2 laser has a long pulse duration and long wavelength, which results in high plasma absorption [37-38]. By devising various unique sampling techniques, we employed the gas plasma method to conduct direct analysis in some delicate soft samples, such as softwoods, powders, and soils [39-42].

We further employed successfully the devised technique for analysis of trace metal on solid material surface of silicon wafer [43]. However, it was confirmed that the technique cannot be used for the sensitive analysis because the material itself (silicon wafer) was ablated when the CO_2 laser irradiates the surface of the silicon continuously. Furthermore, the ablation of the Si material makes the material itself damaged, which is avoided in analysis of trace element on semiconductor material. To overcome this issue, in this present paper, we

proposed new technique of vaporization utilizing a pulse CO_2 laser in laser-induced breakdown spectroscopy for rapid identification and high-sensitivity analysis of trace metal element on material surface (Si wafer) without damaging the material itself, which is necessary in material industries. The technique consists of two steps, namely vaporization and data acquisition. For vaporization, the impurity of trace metal attached on the material surface was vaporized and deposited onto the Pt metal mesh and metal subtarget by defocusing a pulse CO_2 laser beam on the material, which contains trace metal. In the second step, the deposited trace metal elements was then bombarded by a pulse CO_2 laser beam to induce a plasma, obtaining emission spectrum of trace metal element. Using new present technique, rapid identification of trace metal element on material surface can successfully be carried out without damaging the material itself, which is necessary in material industries. The detection sensitivity of impurity element is also high in the order of sub part per million (ppm) level.

2. EXPERIMENTAL PROCEDURE

The material target used in this study was silicon wafers (0.5 mm thick and 51 mm in diameter). The silicon wafers contain Cr at a various concentrations as a

trace element on its surface. For example, to produce Cr film at a concentration of 1.25 mg/kg, the same procedure with the previous experiment [43] was conducted. Namely, 1.25 mg/kg of Cr film was made by the homogeneous dilution of 3.53 mg of $K_2Cr_2O_7$ in 1,000 ml of tap water. Tap water was used because Cr particles can be deposited easily on the surface of a sample. A solution of 0.01% sugar in liquid was also added to the Cr water to attach the trace element to the surface of the sample strongly. Mixed Cr water (1 mL) was poured subsequently onto the surface of the silicon wafer. The wafer was further heated by an electric heater for 5 minutes so that the Cr trace element was dried completely on the surface of the wafer.

Experimental setup used in this work is illustrated in Fig. 1(b) and (c). The setup consisted of two steps, namely new vaporization technique and data acquisition. In vaporization technique, two sheets of platinum metal mesh (wire diameter of 0.12 mm and lattice constant of 0.50 mm) were tightly attached on a copper plate with a dimension of 0.1 x 2 x 2 mm^3. The meshes were then placed at 10 mm in front of the Si wafer, which contains impurity on its surface, as illustrated in Fig. 1(b). The Si wafer was placed on a sample holder, which can be rotated during laser bombardment. The transversely excited atmospheric (TEA)

CO_2 laser (10.64 um, 200 ns, 750 mJ) was directly bombarded and defocused at +5 mm by using a ZnTe lens with a focal length of 200 mm onto the Si wafer surface. The irradiance of the laser beam on the Si wafer surface was 0.09 GW/cm^3. It should be mentioned that no plasma emission was produced during laser bombardment and only the impurity on the wafer surface is vaporized onto the surface of the Pt metal meshes. During laser bombardment, the wafer was continuously rotated with a rotation speed of 2 rotations per minute (rpm). This procedure was made to ensure that the laser beam always attaches new position on the wafer surface and therefore, the impurity optimally vaporizes and moves to deposit and accumulate on the mesh surface. For data acquisition, the meshes on which the impurity is deposited, was placed into the alloy chamber with a diameter of 12 cm. During acquisition, the impurity-deposited mesh was rotated with a rotation rate of 2 rpm. He gas (99.999%) was flown into the chamber with a flow rate of 10 L/min. The pressure inside the chamber was kept constant at 1 atmospheric pressure. The pulse TEA CO_2 laser with a laser energy of 1500 mJ was focused on the mesh surface by using ZnTe lens with a focal length of 200 nm. The irradiance of the laser beam on the mesh surface was 0.75 GW/cm^3. A luminous plasma with a diameter of around 10 mm was then produced just above

the mesh surface.

The plasma emission was collected by an optical fiber, which the end of the fiber was placed at a distance of 30 mm from the plasma region. The other end of the fiber was fed onto an optical multichannel analyzer system (OMA, ATAGO Macs-320, grating of 1200 groves/mm, 1024-channel detector) to obtain an emission spectrum. Each spectrum obtained in this study was executed by laser irradiation (10 shots). The OMA system was set at 10 μs delay time and 200 μs gate width. For plasma emission studies, a delay time was selected at 10 μs. This is because in laser plasma induced by a pulse TEA CO_2 laser (10.64 um, 200 ns, 1500 mJ), the best spectral quality, namely narrow full width at half-maximum (FWHM) and optimum signal to noise (S/N) ratio with low background continuum emission is obtained at around 10 μs [38]. Below 10 μs, the FWHM is still quiet wide and background continuum is still high. The background continuum emission, which is produced by Bremsstrahlung effect (free-free) and recombination (free-bound transition), has long lifetime up to around 10 μs compared to that of plasma emission produced by Nd:YAG laser, which has background continuum emission up to around 1 μs. In laser-induced breakdown spectroscopy (LIBS), FWHM of emission line, S/N ratio, and background

emission determine the spectral quality and thus influence the sensitivity.

3. RESULTS AND DISCUSSION

Very peculiar phenomenon occurs when a pulse TEA CO_2 laser is directed and focused on a material surface, especially on the metal sample. Namely, a large volume and long lifetime plasma was induced without any ablation of the metal surface. The plasma is most often contributed from the surrounding gas, not from the material target, and therefore, we called “gas plasma” as reported in our previous works [38]. By this present method, identification and analysis of impurity in various sample target has been successfully made.

To extend the significance of the method, in this present study, identification of trace metal element on a material Si surface was made. As mentioned in introduction, analysis of trace element on a material surface without any damaging the material itself is very necessary especially in semiconductor industry. At initial study, to avoid the ablation of Si itself by a laser bombardment, a platinum metal mesh (wire diameter of 0.12 mm and lattice constant of 0.50 mm) was employed by tight attaching the mesh on the Si surface and by directing a laser beam onto the Si surface at the angle 25^{o}from the Si surface so that the laser

beam does not directly impinge on the Si surface. The pulse TEA CO_2 laser beam (10.64 um, 200 ns, 750 mJ) was further focused onto the surface of Pt mesh at inclining degree of 25° to induce a luminous plume (Fig. 1(a)). Mixed nitrogen and helium gases with a flow rate of 2.5 liter per minute were flowed during data acquisition process. Figure 2 shows an emission spectrum obtained from the silicon surface containing trace metal element of 1.25 ppm Cr at the wavelength region of 410 nm to 440 nm. Typical neutral Cr lines at the wavelength of 425.4 nm, 427.4 nm, and 428.9 nm are clearly identified together with neutral Ca line at 422.6 nm. Furthermore, a high-intensity broaden emission line at 434.0 nm identified as H_γ line. This result certified that even though the laser beam was sent at the angle of 25° from the Si surface, the Cr impurity deposited on the Si surface still can be vaporized and excited in the plasma region indicated by detection of Cr lines as in the spectrum.

Further experiment was made to confirm whether any ablation happens from the Si surface. As mentioned above, the important goal of the study is to identify and analysis of trace metal element on Si surface without any damage on the Si material itself. Figure 3 displays an emission spectrum taken from the same condition with Fig. 2 at the wavelength region ranging from 270 nm to 310 nm.

Neutral atomic Si line at 288.2 nm faintly appears together with high-intensity neutral He line. The weak line of Si 288.2 nm is most often because of experimental setup, which we proposed in this study, namely, by inclining the laser beam at inclining degree of 25ºcoming onto the Si surface, which is attached by a metal mesh just on the Si surface. By using this technique, the ablation of the material sample can effectively be reduced due to shadow effect by a metal mesh as reported in our previous paper [43]. The existence of Si line verified that the Si material is still ablated by direct laser bombardment in the present method, thus resulting in material damaged. It should be mentioned that when the inclining degree of the metal mesh to the surface of the Si was reduced from 25º to 10º, the emission line of Si at 288.2 nm significantly decreased and almost disappeared, which stated that the ablation of the Si material also decreased. However, the reduction of the Si ablation also reduces significantly the emission lines of Cr impurity at the wavelength of 325.4 nm, 327.4 nm, and 328.9 nm. Therefore, the present technique is not sensitive to be employed for the detection of impurity deposited on the material surface, especially Si surface. Furthermore, this technique cannot effectively be employed to perform analysis of trace element on material without damaging the material itself, which is required in semiconductor

industry.

A new devised technique was then proposed to overcome the problem of the material ablation and reduction of the impurity emission lines. The technique consists of two steps as shown in Fig. 1(b) and (c), namely vaporization and data acquisition. In the first step (Fig. 1(b)), a defocused laser beam at +5 mm was sent onto the Si surface to vaporize the trace element from the Si surface to move on the Pt metal mesh. We confirmed that completely no plasma was induced on the Si surface and no Si emission line at 288.2 nm was detected during defocusing of the laser beam. Also, it should be emphasized that no ablation mark on the Si surface was observed by the microscope. In the data acquisition step (Fig. 1(c)), the trace-element deposited-metal mesh and Cu plate was bombarded by the focused laser beam to induce a luminous plasma and to identify the trace element emission. It should be stated that the metal mesh and Cu plate was not ablated by the laser beam because the power density of the laser beam on their surface is not high enough to ablate the metal as reported in our previous papers [40]. The plasma emission induced was totally contributed from the surrounding gas and the trace element deposited on the surface. We clearly observed the luminous plasma and detected the emission lines of trace element of Cr and H_γ emission as shown

in Fig. 4. The H_γ emission line might be contributed from the sugar solution used during sample preparation process as described in experimental procedure. The sample used was Si wafer containing Cr impurity on the Si surface at 4 ppm. Three typical emission lines of neutral Cr at 425.4 nm, 427.4 nm, and 428.9 nm appears with high intensity and quite low background emission even at low concentration of 4 ppm level. These lines are contributed from the trace element of Cr deposited on the Si surface. In addition, high-intensity and broaden emission line of H_γ at 434.0 nm and neutral Ca line at 422.6 nm contributed from the sugar solution and tap water clearly occurs.

Prior to semi-quantitative analysis of Cr trace element deposited on Si surface, the plasma parameters such as electron temperature and electron density were calculated. By considering the condition of LTE for the population densities of the upper energy levels of two lines is fulfilled, then the intensity ratio method is straight forward for the determination of Te. Considering the intensity of each hydrogen emission spectral line (Balmer region), the electron temperature was calculated using Eq. 1 [44],

$$T_e = \frac{\Delta E}{\ln \frac{[A_1 g_1 \lambda_2 I_2]}{[A_2 g_2 \lambda_1 I_1]} K} \quad (1)$$

Where ΔE, I, λ, g, K and A are the energy difference between two levels, intensity, wavelength, statistical weighting factor, Boltzmann constant and transition probability, respectively. The two hydrogen line transitions for Balmer-γ and for Balmer-δ were used, and the numerical values for the above relation were taken from the NIST database [45]. Based on Eq. 1, the electron temperature was approximately 5000 K. The electron density was determined based on the theory of star broadening, which takes into account quasistatic ion and impact electron broadening effects. The expression for electron density in terms of the linewidth of hydrogen lines is shown in Eq. 2 as follows [46],

$$N_e = 8.02x10^{12}\left[\frac{\Delta\lambda_{1/2}}{\alpha_{1/2}}\right]^{3/2} \quad (2)$$

Where $\Delta\lambda_{1/2}$ is the linewidth of FWHM in angstroms, reduced wavelength $\alpha_{1/2}$ is a function of the electron density and temperature. Precise values of ($\alpha_{1/2}$) for the Balmer series can be found in Ref. [47]. Using Eq. 2, The electron density was estimated to be in the order of 10^{17} cm^{-3}.

Finally, a semi-quantitative analysis of Cr has been carried out by using the Si sample containing various concentrations of Cr on Si wafer surface. Prior to analysis, reproducibility of the gas emission was examined using the ionic He line at 433.8 nm. As shown in Fig. 5, with the number of laser shots at different places on the surface of metal mesh and Cu plate, on which the Cr impurity was deposited, good reproducibility of the He emission is obtained. This graph certified that the plasma produced using this present technique is quite stable and therefore it is feasible for the semi-quantitative analysis of Cr trace element in the Si surface. The good reproducibility of the ionic He line at 433.8 nm was then used as a standard line for making the calibration because the He gas has good stability with different concentration of Cr.

Figure 6 displays the calibration curve for Cr in the Si surface. In this graph, Cr line at 425.4 nm was selected because this line has highest intensity compared to other Cr line. Good linearity with zero intercept was obtained between emission ratio of Cr to He and Cr concentration deposited on the Si surface. Using the same equation for calculating the limit of detection (LoD) as reported here [48], the LoD of Cr was estimated to approximately 100 ppb; The limit of detection was obtained by calculating the signal concentration which yielded 3 times the noise

level because this was clearly identified as a signal that could be distinguished from the noise. This result stated that the present vaporization technique has high possibility to be employed for analysis of Cr impurity deposited on the material surface without ablating the material itself.

4. Conclusion

A vaporization technique consisting of two step process utilizing a pulse TEA CO_2 laser has been developed and demonstrated for the identification impurity element of Cr deposited on material surface of Si. Good stability of the plasma emission was examined. Using the present technique, a semi-quantitative high-sensitivity analysis of Cr impurity deposited on a Si surface without ablating the Si material was successfully made. A good linearity calibration curve of Cr using ionic He line as a standardization with an intercept zero was demonstrated. The limit detection of Cr was approximately 100 ppb. The present technique is potentially applied to high-sensitivity analysis of impurity on material surface in material science and industry.

Acknowledgments

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Figure captions

Fig. 1 Illustration of Experimental setup used in this study (a) by inclining technique, (b) and (c) by vaporization technique.

Fig. 2 Emission spectrum of Cr deposited on the surface of silicon wafer containing 1.25 ppm Cr using inclining technique

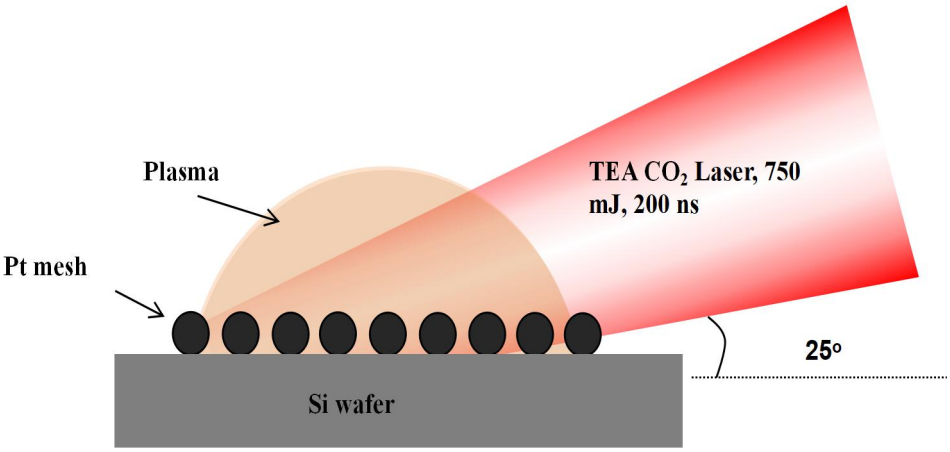
Fig. 3 Emission spectrum of Si taken from the Si wafer containing Cr at 1.25 ppm using inclining technique

Fig. 4 Emission spectrum of Cr obtained from the Si wafer surface containing Cr at 4 ppm using vaporization technique

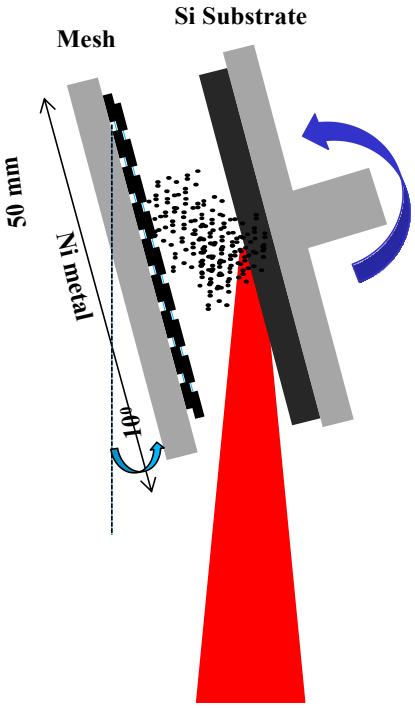
Fig. 5 Reproducibility of He emission obtained from the gas plasma produced on the surface of Si wafer containing 4 ppm Cr

Fig. 6 Calibration curve of Cr deposited on the Si surface at various concentrations by using the vaporization technique

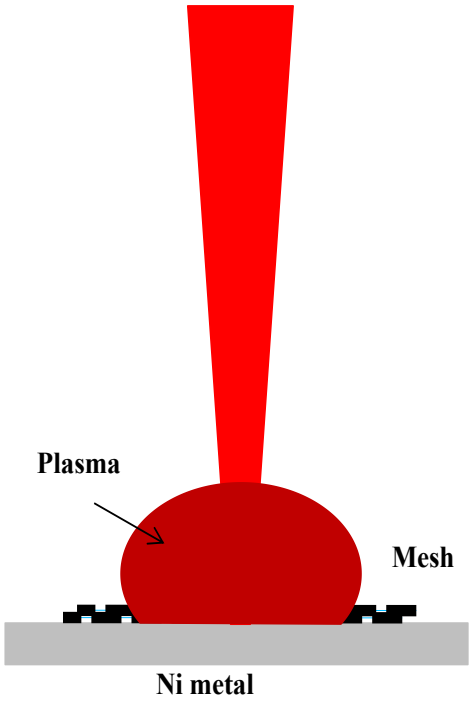
Figure 1
Experimental setup used in this study



(a)



(b)



(c)

Figure 2
Emission spectrum of Cr deposited on a surface of silicon wafer containing 1.25 ppm Cr

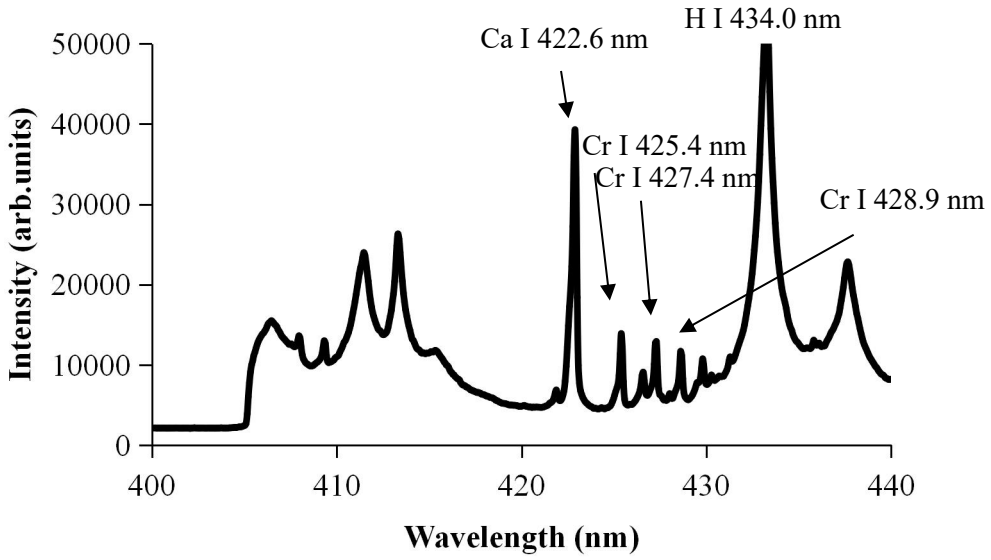


Figure 3

Emission spectrum of Si taken from the Si wafer containing Cr at 1.25 ppm

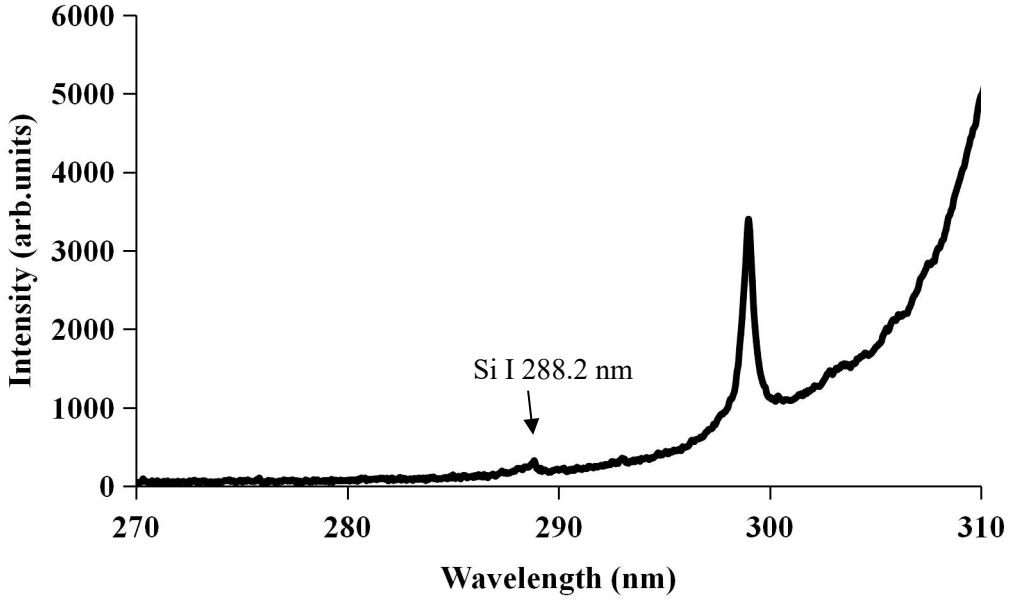


Figure 4
Emission spectrum of Cr obtained from the Si wafer surface containing Cr at 4 ppm using vaporization technique.

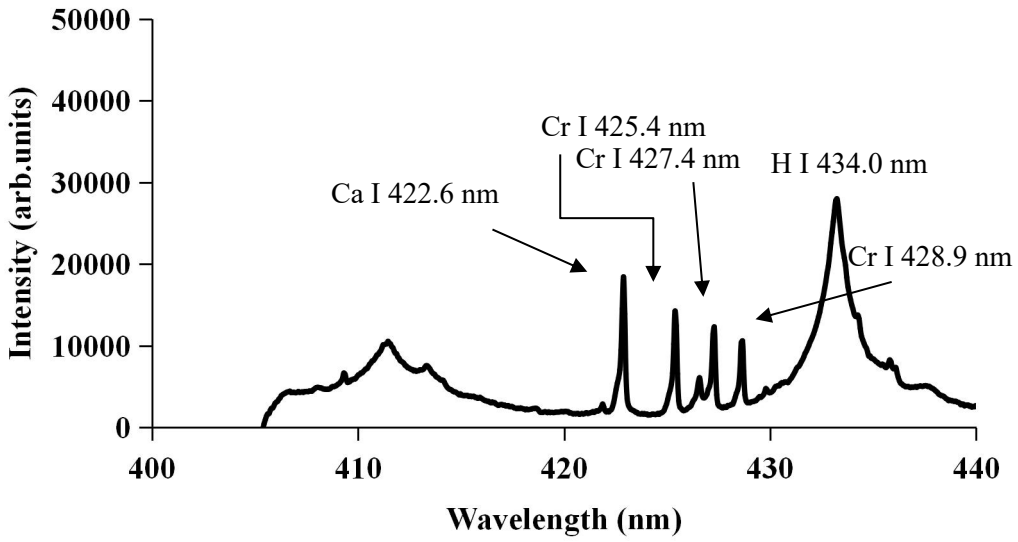


Figure 5

Intensity ratio of Cr and H emission obtained from the plasma produced on the surface of Si wafer containing 2 ppm Cr.

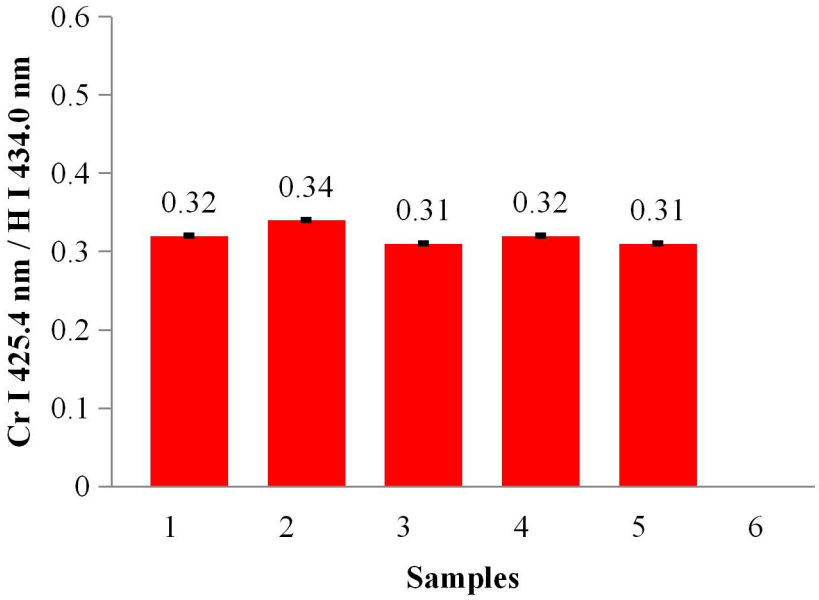
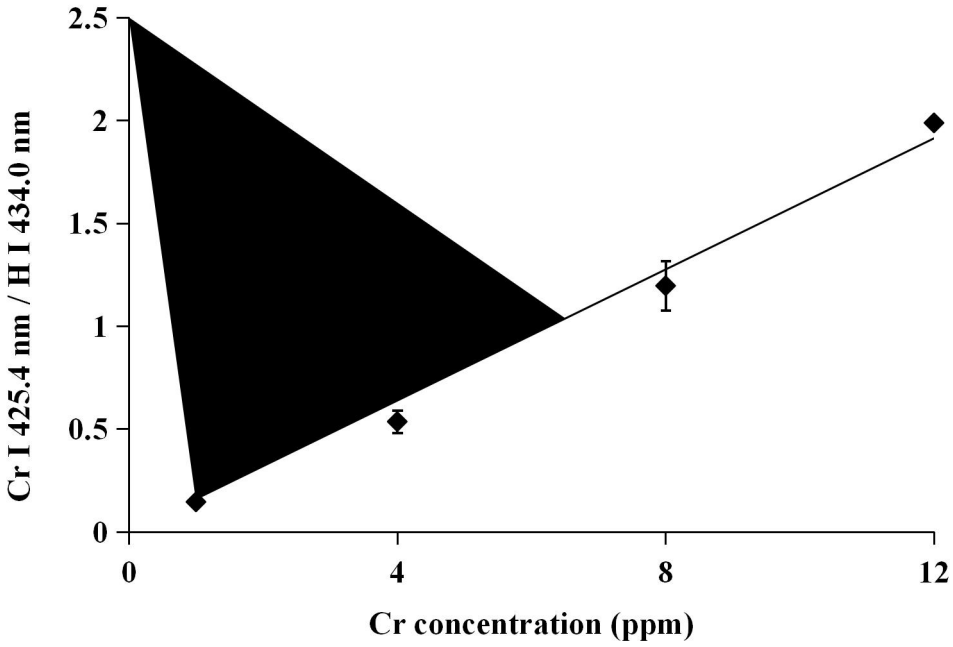


Figure 6

Calibration curve of Cr deposited on the Si surface at various concentrations by using the vaporization technique



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